UNIVERSITY OF RUHUNA

BACHELOR OF SCIENCE GENERAL DEGREE LEVEL I (SEMESTER I) EXAMINATIONS – AUGUST 2017

SUBJECT : CHEMISTRY

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

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 $^{-1}$
Avagadro's number, (N_A)	$= 6.022 \times 10^{23}$ mol $^{-1}$
Universal Gas Constant, (R)	$= 8.314 \times$ 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
Proton 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

Answer **all** parts.

(a) (i) Calculate the total number of orbitals associated with the principal quantum number 4.

(15 marks)

(ii) Sketch the shapes of the $d_{x^2-y^2}$ and d_{z^2} orbitals.

(05 marks)

(iii) Match the following processes with the relevant electron affinities. Justify your answers.

Process	Electron affinity (kJ mol^{-1})
(I) $O^-(g) + e \rightarrow O^{2-}(g)$	(A) - 348
(II) $F(g) + e \rightarrow F^-(g)$	(B) + 844
(III) $Cl(g) + e \rightarrow Cl^-(g)$	(C) - 333

(15 marks)

(b) (i) Arrange the following in the increasing order of the given property. Give reasons for your answers.

(I)	Radius	Ca, K^-, Sc^+
(II)	Covalent property	CuO, CuS
(III)	Boiling point (^oC)	HBr, Cl_2, F_2

(25 marks)

(ii) Give reasons for the following observations:

(I) Se and S are elements that belong to the same group in the Periodic Table. SeO_2 is a solid while SO_2 is a gas.

(II) The melting point of NaCl is very much higher than that of $AlCl_3$.

(III) KCl is an ionic compound. However, solid KCl does not conduct electricity.

(15 marks)

(c) (i) Using the Slater's rules calculate the effective nuclear charge for a 2p electron in the Na^+ ion.

(20 marks)

(ii) Draw the structure of graphite and label it's covalent bonds and van der Waal forces.

(05 marks)

02. Answer **all** parts.

(a) What are the main assumptions of the Bohr model of the atom?

(15 marks)

(b) Calculate the ionization potential (I, in eV) of the hydrogen atom.

According to the Bohr theory, the energy of an electronic energy level in the hydrogen atom is $E_n = -\frac{me^4}{8\varepsilon_0^2 n^2 h^2}$; Where,m = mass of an electron, e = charge of an electron, h = Planck's constant, ε_0 = vacuum permittivity and n = energy level

Note:

$1eV = 1.60218 \times 10^{19}\ J$ $\quad \varepsilon_0 = 8.85418 \times 10^{-12}\ C^2\ J^{-1}\ m^{-1}$

(35 marks)

(c) "Four electron pairs around the central atom lead to three different molecular geometries". Justify the above statement.
Give an example for each geometry.

(15 marks)

(d) Predict the hybridization and the geometries of following molecules:

(i) SF_4
(ii) ClF_3
(iii) XeF_2
(iv) IF_5
(v) XeF_4

(25 marks)

(e) Using the Molecular Orbital theory explain why NO^+ is more stable than NO^-

(10 marks)

Answer **all** parts

(a) Neutron is made up of three quarks and they are up and down quarks. A student has mentioned that a neutron has an up quark and a down quark. What is the missing quark? Give reason(s) for your answer.

(15 marks)

(b) (i) List the four types of fundamental forces and relevant force carrier particles in the following table:

Fundamental force	Relevant force carrier particle

(15 marks)

(ii) Answer the following questions based on the answers you have given for (b) (i) above.

(I) Which force carrier particle(s) has/have an electrical charge?
(II) Which fundamental force(s) is/are effective in the shortest range?
(III) Which fundamental force(s) is/are affected by the colour charge?
(IV) Which type of fundamental force holds the quark particles together to form baryons?

(20 marks)

(c) According to the Liquid drop model for atomic nuclei, the nucleus of an atom resembles a drop of liquid in many respects.

(i) Sate five factors which support the liquid drop model for atomic nuclei.

(15 marks)

(ii) What are the weaknesses of this model?

(05 marks)

(d) Naturally occurring oxygen consists of three isotopes ^{16}O, ^{17}O and ^{18}O.

(i) Giving reasons, arrange the above isotopes in increasing order of their stability.

(15 marks)

(ii) Justify the answer, given for (d)(i) above by comparing the binding energy per nucleon for ^{16}O, ^{17}O and ^{18}O. Observed mass of ^{18}O is 17.9992 amu and the binding energy per nucleon for ^{16}O and ^{17}O are 7.72 MeV and 7.51 MeV respectively.

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.

(15 marks)

Section - B

04. Answer **all** parts

(a) (i) "Two valency carbon is **not** the commonly available form of carbon", giving reasons, explain this statement.

(ii) State how the valency of carbon is associated to form large number of organic compounds.

(10 marks)

(b) Giving reasons, arrange the following molecules in the order of increasing their boiling point:

$C_2H_5OC_2H_5$, CH_3CHO, CH_3CH_2OH, $CH_3CO_2CH_2CH_3$

(15 marks)

(c) (i) Draw the Lewis structure of ClO_3^- ion.

(ii) Calculate the formal charge of each atom of the above ion and assign them.

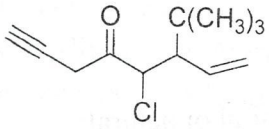
(iii) Comment on the stability of ClO_3^- based on the theory of resonance.

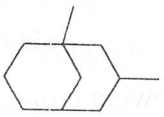
(25 marks)

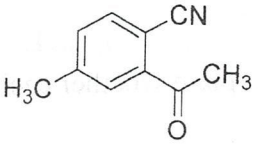
(d) Apply the concept of electronic effects to compare the acidity of CH_3COOH and CH_3OH.

(20 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) 2,5,5-Trimethyl-4-oxo-2-heptenoic acid

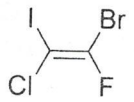
(ii) Ethyl 3-(4-methoxy-2-oxo-3-cyclohexenyl)propanoate.

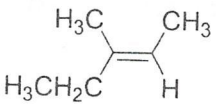
(iii) 5-Amino-3-methyl-2-pentanol

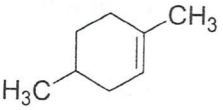
(15 marks)

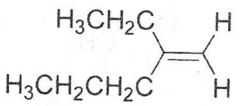
5. Answer **all** parts

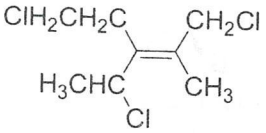
(a) (i) Which of the following compounds show geometrical isomerism? Give reasons to your answer.

(I) 

(II) 

(III) 

(IV) 

(V) 

(16 marks)

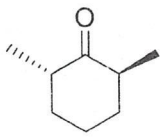
(ii) Giving reasons assign the E/Z configurations to the above compounds which show geometrical isomerism.

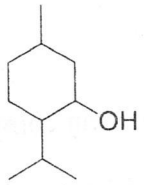
(20 marks)

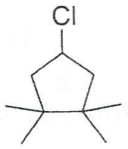
(b) Both alkenes $ClCH{=}CHCH_3$ and 2-butene show geometrical isomerism. Among the E and Z isomers of $ClCH{=}CHCH_3$, E isomer has higher dipole moment while the Z isomer has the higher dipole moment in the case of 2-butene. Explain.

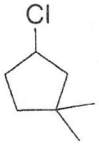
(14 marks)

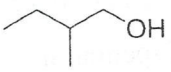
(c) Explain whether each of the following molecules is chiral or achiral:

(I) 

(II) 

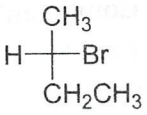
(III) 

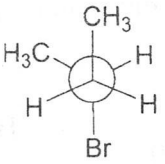
(IV) 

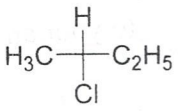
(V) 

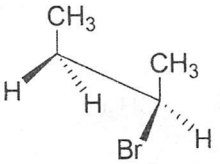
(20 marks)

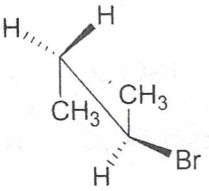
(d) Giving reasons, assign R or S configurations to the following compounds:

(I) 

(II) 

(III) 

(IV) 

(V) 

(30 marks)

06. Answer **all** parts

(a) Define following terms related to organic molecules.

(i) Conformations (ii) Angle strain

(10 marks)

(b) (i) Draw the possible conformations of propane using Newman projection formula.
(ii) Mark the dihedral angle in each projection.
(iii) Draw the potential energy diagram for propane.

(30 marks)

(c) (i) Draw two possible chair confirmations for *cis* 1-chloro-4-*t*-butylcyclohexane

(ii) Giving reasons compare the stability of the confirmations mentioned in the part (c) (i) .

(25 marks)

(d) When cyclohexane is substituted by an ethynyl group , ($^{-}C{\equiv}CH$), the Gibbs free energy difference, $\Delta G°$(axial-equatorial), is -1.7 kJ mol^{-1}. For methyl cyclohexane that value is -7.28 kJ mol^{-1}.

(i) Calculate the ratios of equatorial-substituted to axial-substituted conformations for the given compounds at 25 °C.

(ii) Comparing the conformational equilibrium for methylcyclohexane with that of ethynylcyclohexane and account for the difference between two.

Hint: The Gibbs free energy difference at equilibrium is given by

$$\Delta G° = -RT \ln K_{eq}$$

(35 marks)

Section - C

07. Answer **all** parts

(a) (i) Derive the SI units of power using basic SI units.

(ii) Write down the van der Waals equation for n number of moles of a real gas and give a short account on it.

(20 marks)

(b) The kinetic molecular theory of ideal gases is based on five (5) major assumptions.

(i) State them.

(ii) Write down the limitations of kinetic molecular theory.

(20 marks)

(c) (i) Write down the mathematical equations for the mean speed ($\bar{c}$) and the most probable speed (c_p) of gas molecules of an ideal gas and distinguish between them.

(20 marks)

(ii) The collision frequency and the collision diameter of a certain ideal diatomic gas molecules at 25 ^{0}C and 1 nTorr are 1.06 x 10^{-2} s^{-1} and 395 pm respectively.

(I) Calculate the mean speed ($\bar{c}$) of the molecules of the gas.

Note: 1 Torr =101325/760 Pa

(25 marks)

(II) Identify the gas using a suitable calculation.

(15 marks)

08. Answer **all** parts

(a) The interpretation of colligative properties can be made using the temperature dependence of the chemical potential of a pure substance. The variation of chemical potential with temperature equals to the negative value of the entropy of the substance.

(i) State the major assumptions one should make on explaining the colligative properties.

(10 marks)

(ii) Sketch the graph of chemical potential of a pure solvent vs the temperature covering three physical states.

(20 marks)

(iii) Sketch a graph for the variation of chemical potential of a solution with the temperature and explain the importance of assumptions made in part (i) above.

(20 marks)

(b) Some molecules may either dissociate or associate when dissolve in a solvent depending on the relative polarity of the solvent. Variation of the colligative properties is a measure of the extent of dissociation or association. Sulphur (S) in naphthalene solvent associates as shown below.

$$nS \longrightarrow S_n$$

(i) Construct an expression for the actual molar mass of sulpur with respect to the calculated molar mass.

(10 marks)

(ii) Cryoscopic constant of Naphthalene is 6.5 K kg mol^{-1}. 3.94 g of sulphur was dissolved in 100 g of naphthalene by heating to its melting point at 81.0 ^{o}C. As a result, freezing point of the mixture was lowered to 80.0 ^{o}C. Calculate the value of *n* given in the equation.

(40 marks)

19. Answer **all** parts

(a) A 0.6820 g sample of an unknown weak monoprotic organic acid, HA, was dissolved in sufficient amount of water to make 50.00 mL solution and was titrated with a 0.1350 mol dm^{-3} NaOH solution. After the addition of 10.60 mL of base, pH of the solution was measured to be 5.65. The end point was reached after the addition of 27.40 mL of base. Calculate the following.

(i) The number of moles of acid in the original sample.

(ii) The molecular weight of the acid HA.

(iii) The number of moles of unreacted HA remaining in solution when pH was 5.65.

(iv) The $[H_3O^+]$ at pH = 5.65

(v) The value of the ionization constant, K_a, of the acid HA.

(vi) The standard Gibbs free energy change for this reaction at 25 ^{0}C. ($K_w = 1 \times 10^{-14}$)

(50 marks)

(b) (i) Define the term precision.

(ii) What are the two types of precision?

(iii) Which type of error(s) affects the precision most?

(iv) What are the statistical terms used to express the precision?

(25 marks)

(c) An analytical method should give a relative standard deviation of 6 ppt or better. A sample was first analyzed three times using this method to give the following set of results: 43.22%, 43.25%, and 43.65%. Because the result 43.65% appears questionable, two additional results were obtained as follows: 43.30% and 43.49%.

(i) Calculate the standard deviations of the first set (n = 3) and of the complete set (n = 5).

(ii) Evaluate the precision of each of the two sets of results.

(25 marks)

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