UNIVERSITY OF RUHUNA

BACHELOR OF SCIENCE IN FISHERIES AND MARINE SCIENCES DEGREE

EXAMINATION, January 2016

LEVEL I, SEMESTER II

FSC 1b14 – Foundation course on Chemistry for Aquatic Sciences – I (Theory)

Time: 3 hours

Answer only **SIX (06)** questions by selecting question number **01** and **ONE (01)** from each of the parts **A**, **B** and **C** and **TWO (02)** from the part **D**

Velocity of light (c)	= 3×10^{8} ms^{-1}
Planck's constant (h)	= 6.626×10^{-34} Js
Mass of electron (m_e)	= 9.10×10^{-31} kg
Charge of electron (e)	= -1.602×10^{-19} C
Mass of Proton (m_p)	= 1.673×10^{-27} kg
Universal gas constant (R)	= 8.314 J K^{-1} mol^{-1}
Avogadro constant (N_A)	= 6.022×10^{23} mol^{-1}
Faraday constant (F)	= 9.6485×10^{4} C mol^{-1}
Boltzmann constant (k)	= 1.381×10^{-23} J K^{-1}
1 amu	= 1.661×10^{-27} kg = 931.454 MeV
1eV	= 1.602×10^{-19} J

01. Answer **all** parts.

a) i) Define *Aufbau* Principle.

ii) Electronic configuration of Cu and Cr do not follow *Aufbau* Principle. Expalin?

(10 Marks)

b) i) Draw the shapes of 2Px, 2Py, and 2Pz- orbitals.

ii) Give all the possible quantum numbers for an electron in 2s, 3d, and 4p orbitals.

(15 Marks)

c) Calculate the energy released during the transition of an electron in a hydrogen atom from the energy state n=5 to n=1. Planck's constant, Rydberg constant and velocity of light are respectively 6.626 $x10^{-34}$ Js, 1.09737 $x10^{7}$ m^{-1}, and $3x10^{8}$ ms^{-1} respectively.

(20 Marks)

d) The bond angles of CH_4, NH_3, and H_2O are 109.5°, 107.0°, and 104.5° respectively. Explain this difference using VSEPR theory.

(15 Marks)

e) i) Overlapping of two s- orbitals can only form a σ-bond but not a π-bond. Explain?

(10 Marks)

ii) Using a suitable molecular orbital diagram show that the bond order of He_2 molecule is zero.

(10 Marks)

iii) "O_2 molecule is attracted by an external magnetic field". Explain this statement considering the magnetic properties of O_2 molecule and using the molecular orbital energy level diagram.

(10 Marks)

PART – A

02. Answer **all** parts.

a) Arrange the following carbonates in increasing order of thermal stability.

$CaCO_3$ $BeCO_3$ $BaCO_3$ $SrCO_3$ $MgCO_3$

(10 Marks)

b) Define, "*standard hydration enthalpy of a cation*" and give two factors on which the standard hydration enthalpy of a cation depends.

(20 Marks)

c) Propose the products for the following reactions using balanced equations.

i) Thermal decomposition of $NaNO_3$.

ii) B_2H_6 with water.

iii) Phosphorus with conc. HNO_3.

iv) MnO_4^- with NO_2^- in an acidic medium.

(05 × 4 Marks)

d). Explain the following observations.

i) I_2 is slightly soluble in water and the addition of KI increases its solubility.

ii) H_2O is a liquid and H_2S is a gas under ambient conditions.

(20 Marks)

e) Draw the structures of the following

i) XeF_4

ii) $H_2S_2O_7$

(16 Marks)

f) Explain the extraction of **Boron** from H_3BO_3. (Provide chemical equations wherever applicable)

(14 Marks)

03. Answer **all** parts

a) Define "Transition element".

(05 Marks)

b) List major properties of "d-block" elements.

(10 Marks)

c) Use following d-block complexes and compounds to answer the questions,

$[Cr(OH)_6]^{3-}$ $Fe(CO)_5$ V_2O_5 $[Co(NH_3)_5Cl]^{2+}$

i) Provide IUPAC names.

ii) Give the oxidation number of the transition metal ion.

iii) Provide the geometry of $Fe(CO)_5$ molecule. (*Note*: You could use VSEPR theory to predict the geometry of a molecule)

(25 Marks)

d) Providing chemical equations, write down the products of the following reactions.

i) Aqueous NaOH with $CuSO_4$.

ii) Zn with excess NaOH.

iii) ZnS with dilute HCl.

(18 Marks)

e) Consider the following table,

Sn	**HF**	**H_3PO_4**	**Cl_2O_7**	**Ni^{2+}**	**Pr**

i) Identify the substance(s) which react with both HCl and NaOH to produce H_2.
Write the balanced equations for each reaction you selected.

ii) Giving reasons identify the most acidic substance(s) in aqueous medium.

iii) Select the substance which is a lanthanide.

iv) Select the compound(s) which gives a dark blue solution in excess dil. NH_3 and draw the structure of this species.

(20 Marks)

f) Relationship between the half- life of a radioactive element ($t_{1/2}$) and the decay constant is given by $t_{1/2} = 0.693/ k$. The radioactive decay constant (k) of a radioactive element is found to be 0.005 min^{-1}. Calculate the time taken for 25% of the initial mass of a sample of that element to decay. (22 Marks)

PART – B

04. Answer **all** parts

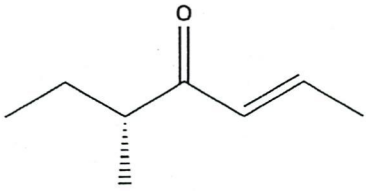
a) Define Followings,

i) "Enantiomers"

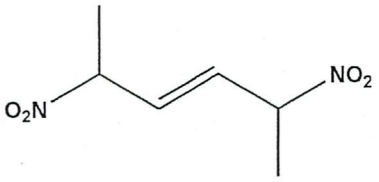
ii) "Diastereomers"

(12 Marks)

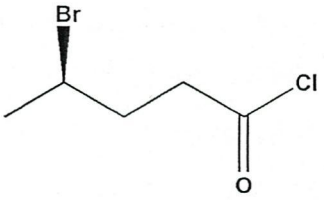
b) Consider the following molecules



A



B



C

i) Give *IUPAC* names of above molecules.

(12 Marks)

ii) Identify the chiral molecule(s) out of above molecules.

(06 Marks)

iii) Draw geometrical isomers for **A** and identify the type of geometrical isomerism present there.

(10 Marks)

iv) Draw the lowest energy *Numann projections* through **C2-C3** bond of the molecule **C** and show the lowest energy projection formula.

(10 Marks)

v) Draw the *Fischer projection* for molecule **C** and assign "**R**" and "**S**" designations for chiral center(s).

(10 Marks)

c) Briefly explain following observations.

i) "Envelope conformation of *cyclopentane* is more stable than its planar conformation".

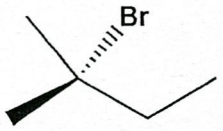
ii) "The ratio of ***axial**-tertiarybutylcyclohexane* to ***equatorial**-tertiarybutylcyclohexane* is 03% to 97%".

(16 Marks)

d)

i) Draw the structures of the product(s) formed in the following reaction.

ii) Give the possible mechanism for the formation of product in (i)



Sodiumethoxide (EtO^-Na^+)

Ethanol

(11 Marks)

e) Explain, why polar protic solvents are excellent for ***S_N1 reactions*** whereas polar aprotic solvents for ***S_N2 reactions***.

(12 Marks)

05. Answer **all** parts

a) Explain the following.

i) "Mesomeric effect"

ii) "Inductive effect"

(20 Marks)

b) Briefly describe the stability of **tertiary**, **benzilic** and **allylic** *carbocations* using suitable examples. (*Note*: Use above terms for your explanation)

(15 Marks)

c) Briefly rationalize following.

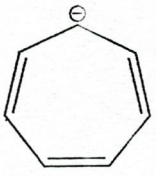
i) Stability of the "*Annulenes*"

ii) *Pyridine* is more basic than *pyrrole.*

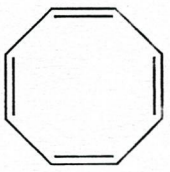
iii) *Phenol* is more acidic than aliphatic *alcohols.*

(26 Marks)

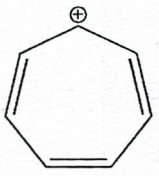
d) Explain the aromaticity of following molecules using Huckel Rule.



A



B

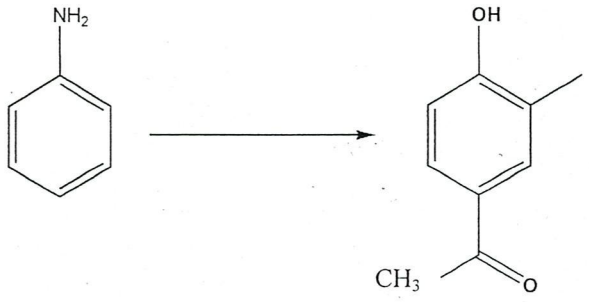


C

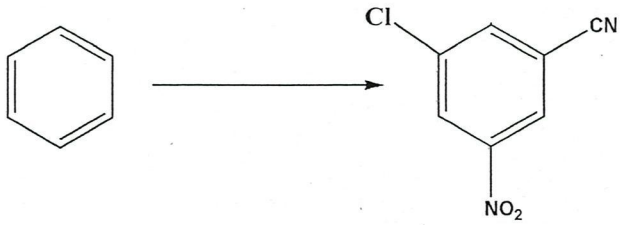
(15 Marks)

e) Indicating necessary reagents and reaction conditions, show how you would carry out following conversations.

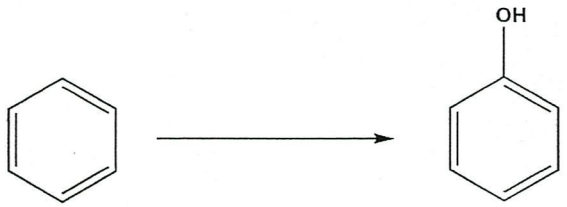
i)



ii)



iii)



(08 × 3 Marks)

PART – C

06. Answer **all** parts.

a) Briefly explain the following.

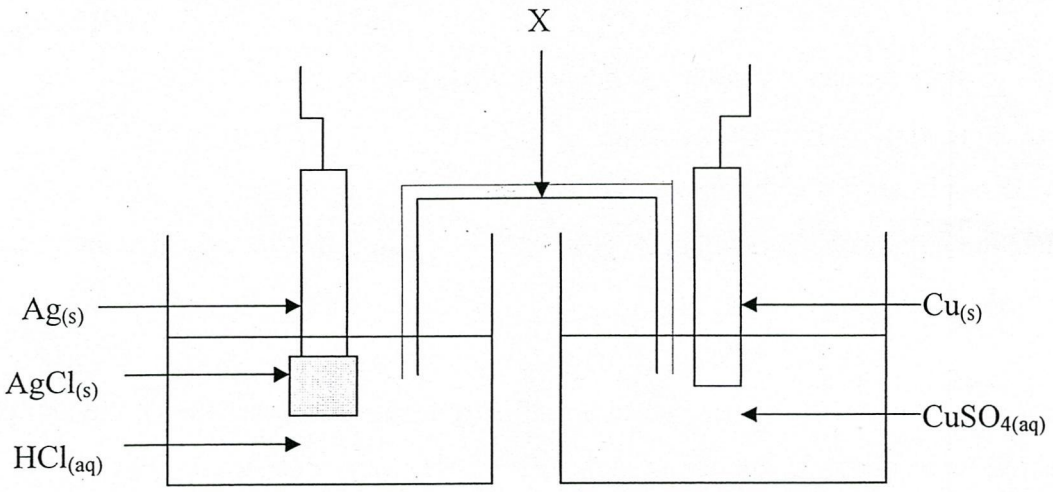
i) Electrolytes.

ii) Metal insoluble salt electrode.

iii) Primary standard electrode.

(05 × 3 Marks)

b) Use the following diagram of an electrochemical cell to answer the questions.



i) Give the following with respect to the diagram.

A. Electrode reactions.
B. Cell reaction.
C. Cell notation.

ii) Identify the part labeled as "X".

iii) Explain what is meant by "*liquid junction potential*". How would you overcome the problem associated with it?

(12 Marks)

c) The Nernst equation,

$$E = E^{o} - \frac{2.303RT}{nF}\log Q$$

i) Identify all the terms in the above equation.

ii) Write down an expression for **Q** as applied to the following reaction.

$$Cu^{2+}\ (aq) + \ 2Ag(s) \longrightarrow Cu(s)\ +\ 2Ag^{+}(aq)$$

iii) Use the above reaction to provide a specific term for **Q** which can be used for dilute solutions.

iv) A cell operating at 298 K consists of a Zn^{2+} / Zn electrode and a Ni^{2+} / Ni electrode. Calculate the cell potential, if $[Zn^{2+}] = 0.125$ mol dm^{-3} and $[Ni^{2+}] = 0.628$ mol dm^{-3}.

Note: $E^{o}_{Zn^{2+}/Zn} = -0.76\ V$ *and* $E^{o}_{Ni^{2+}/Ni} = -0.25\ V$

(23 Marks)

d) Briefly describe how the order of a reaction can be determined by differential rate law.

(10 Marks)

e) Dissociation of the substance "**A**" follows second order kinetics.

i) Derive an expression for the rate constant.

ii) Graphically represent the above expression.

iii) Calculate the initial concentration of A. (Use 1.23×10^3 dm^3 mol^{-1} as the intercept of the graph)

(20 Marks)

f) Thermal decomposition of X is observed to be a first order reaction. At 105° C, the plot of rate versus [X] gives a straight line with a slope of 1.95×10^{-3} dm^3 mol^{-1} s^{-1}.

i) Show that the half life of a first order reaction,

$$t_{1/2} = 0.693/ k$$

ii) Calculate the half life of the reaction.

(20 Marks)

07. Answer **all** parts.

a) State **five** basic steps of a surface catalyzed chemical reaction.

(15 Marks)

b) When a gas is in contact with a catalytic surface, following equilibrium is established.

$$\mathbf{S^* + M} \rightleftharpoons \mathbf{S\text{-}M}$$

Where,

S* = Concentration of empty surface sites
M = Concentration of gas molecules
S-M = Concentration of filled surface sites

i) Show that the coverage (θ) is given by,

$$\theta = \frac{K p}{1 + K p}$$

Where, K is the equilibrium constant and p is the pressure of the gas.

ii) Give *three* assumptions you used to derive above expression.

iii) Sketch the variation of Q versus P.

iv) Following table shows data for adsorption of CO on charcoal at 273 K. Find the equilibrium constant K.

CO gas pressure / kPa	Volume corresponding to the coverage at STP (1.01×10^5 Pa, 98 K) / cm^3
13.3	10.2
26.7	18.6
40.0	25.5
53.3	31.5
66.7	36.9
80.0	41.6
93.3	46.1

(40 Marks)

c) There are two types of solvent properties which depend upon the solute and solutions known as *colligative* and *none colligative* properties.

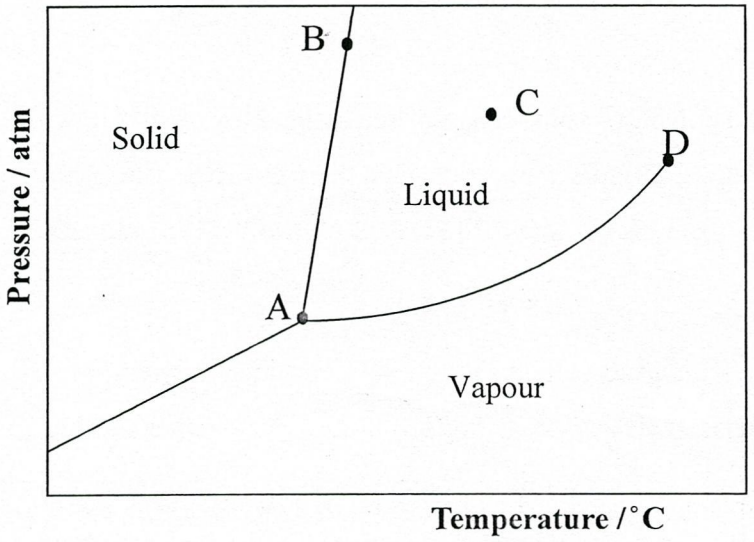
i) Providing suitable examples, differentiate *colligative* and *none colligative* properties.

ii) Give two useful applications of *colligative* properties.

iii) Calculate the weight of $CaCl_2$ need to be added in order to increase the boiling point of 2 kg of pure water to 105° C. (K_b for water is 0.51° C kg mol^{-1})

(25 Marks)

d) Phase diagram of water is given bellow.



i) Identify the points A and D.

ii) Define the number of degrees of freedom in the context of phase equilibrium.

iii) Calculate the number of degrees of freedom at each point A, B and C.

(20 Marks)

PART – D

08. Answer **all** parts.

a) Define

i) "*Molality" and "Molarity"*

ii) "*Percent composition*" and "*Mole fraction*"

(10 × 2 Marks)

b) What is the density of 54.3 wt% aqueous NaOH (MW= 40.00) if the dilution of 17.6 mL of this solution to 2.00 L produced 0.196 M NaOH solution.

(16 Marks)

c) For the following calculations, determine the answer with the appropriate uncertainty for each result. (*Note*: (If, y = x_1 + x_2 ; uncertainty $e_y = \sqrt{x_1^2 + x_2^2}$, If, y = log (x) ; $e_y = \frac{1}{\ln 10}\frac{e_x}{x}$, Provide the answer with proper number of *significant figures*)

i) 6.4 (±0.2) - 3.0(±0.2)

ii) -log 4.70 (±0.2) x 10^{-6}

(16 Marks)

d) The molarity of an NaOH solution was determined by titration with KHP (Potassium Hydrogen Phthalate). Individual titrations gave the following concentrations.

(0.1127, 0.1126, 0.1132, 0.1174 and 0.1173) mol dm^{-3}

i) Write your opinion on *"precision"* of the above results

ii) Identify *any rejectable data points* at the 90% confidence interval

(**Note**: **Qcrit** = ($|x_q - x_n| / x_{higest} - x_{lowest}$), where x_q = questionable result and x_n = the nearest neighbor of the questionable result; Outliers could be identified if **Qexp > Qcrit**)

Number of observations (N)	3	4	5	6	7	8
Qcrit at CL 90%	0.941	0.765	0.642	0.560	0.507	0.468

iii) Find the *"mean"* and *"standard deviation"*.

iv) Find the "relative standard *deviation*".

v) Compute the "relative standard *deviation*" in ppt.

vi) Provide the concentration of NaOH in reportable format.

(08 × 6 Marks)

09. Answer Either **A** or **B**

A] Answer **all** parts

a) Define,

i) "*Chelate*"

ii) "*Conditional formation constant*"

(10 × 2 Marks)

b) Briefly discuss "use of indicators in *complexometric titrations*"

(15 Marks)

c) Calculate the equilibrium concentration of Ni^{2+} in a solution with an analytical NiY^{2-} concentration of 0.0150 M at following pH,

(*Note*: $K_{NiY} = 4.2 \times 10^{18}$, $\alpha_{Y^{4-}} = 2.5 \times 10^{-11}$ and 5.4×10^{-3} at pH = 3 and 8 respectively)

i) 3.0

ii) 8.0

(25 Marks)

d) A 100.00 mL aliquot of municipal drinking water was treated with a small amount of ammonia – ammonium chloride buffer to bring the pH to 10. After the addition of an indicator, the solution required 21.46 mL of 5.140×10^{-3} M Ethylenediaminetetraacetic acid (EDTA) for titration.

i) Suggest a suitable indicator for the above titration.

ii) Clearly indicate the colour change of the indicator you suggested.

iii) Calculate the hardness in terms of parts per million calcium carbonate.

iv) Write your opinion on addition of 1.0 mL of Mg-EDTA complex to the above analyte.

v) Draw the structure of Ca-EDTA complex. (*Note:* EDTA has four carboxyl groups and two amine groups that can act as Lewis bases.)

vi) Write the coordination number and geometry of the above complex.

vii) Comment on the direct titration of Calcium ions in a sample.

(40 Marks)

B] Answer **<u>all</u>** parts

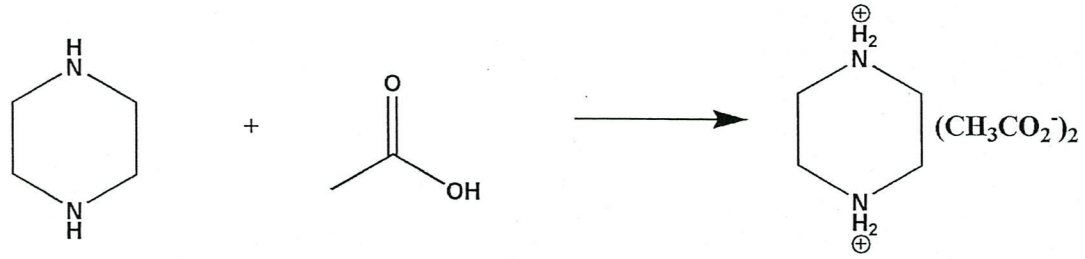
a) Explain the difference between,

i) "Nucleation" and "Particle growth"

ii) "Relative supersaturation"

(10 × 2 Marks)

b) The piperazine content of an impure commercial material can be determined by precipitating and weighing the diacetate product.



Piperazine M = 86.08 **Acetic acid M = 60.05** **Piperazinediacetate M = 206.24**

In an experiment, 0.3126 g of sample was dissolved in 25.00 mL of acetone and 1 mL of acetic acid was added. After 5 min, the precipitate was filtered, washed with acetone, dried at 110 °C, and found to weigh 0.7121 g. Find the wt% of piperazine in the sample.

(20 Marks)

c) *Henderson–Hasselbalch equation* describes the derivation of pH as a measure of acidity in biological and chemical systems. The equation is also useful for estimating the pH of a buffer solution and finding the equilibrium pH in acid-base reactions.

i) Give an example for acidic buffer solution.

(08 Marks)

ii) Briefly explain buffer action of the example you proposed.

(11 Marks)

(12

iii) Derive the *Henderson–Hasselbalch equation* for the same buffer system.

(10 Marks)

iv) Express the pH of a buffer system in terms of the dissociation constant of the weak acid where, the ratio of concentrations of the weak acid and the conjugate base are 1:5.

(10 Marks)

v) Calculate the volumes that required to produce a buffer solution having pH 5.00 if you are provided with a weak acid (HA) and its conjugate base (A^-) both having 0.1000 mol dm^{-3} concentration. ($Ka_{(HA)} = 1.74 \times 10^{-5}$)

(12 Marks)

vi) Give two applications of acidic buffer solutions.

(08 Marks)

@@@@@@@@@@