UNIVERSITY OF RUHUNA

BACHELOR OF SCIENCE IN FISHERIES AND MARINE SCIENCES DEGREE EXAMINATION, January, 2017

Level I, Semester II

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

Time: 3 hours

Answer either **Part 'A'** or **Part 'B' of the question number 1**

PART 'A'

1A. Answer **all** parts

(a) (i) Consider the following reaction.

$$M^{n+} + Y^{4-} \rightleftharpoons MY^{n-4}$$

Using the relationship $[Y^{4-}] = \alpha_{Y^{4-}}[EDTA]$ show that $K_f' = \dfrac{[MY^{n-4}]}{[M^{n+}][EDTA]}$

Where K_f' is the conditional or effective formation constant at a given pH.

(15 marks)

(ii) Calculate the conditional formation constant K_f' for CaY^{2-} complex at pH =10

Note: For Ca^{2+} $\log K_f = 10.65$, $\alpha_{Y^{4-}} = 0.30$ for EDTA at pH = 10

(10 marks)

(b) (i) Briefly discuss how you would perform back titrations in complexometric determination of metal ions.

(15 marks)

(ii) Under what conditions you would perform back titrations?

(10 marks)

(iii) 25.00 mL of 0.0502 M EDTA is added to a 50.00 mL of a solution prepared by dissolving an alloy containing Ni. Titration of unreacted EDTA requires 12.05 mL of 0.0540 M Zn^{2+} solution. Calculate the concentration of Ni(II) in the solution.

(15 marks)

(c) Following table shows some stability constants (K_{MY}) for the formation of metal-EDTA complexes. Giving reasons answer the following questions.

Metal ion	K_{MY}
Mg^{2+}	4.9×10^{8}
Pb^{2+}	1.1×10^{18}
Ba^{2+}	5.8×10^{7}
Cu^{2+}	6.3×10^{18}

(i) What reaction will occur if a solution containing Pb^{2+} is added to a solution containing MgY^{2-}?

(10 marks)

(ii) What reaction will occur if a solution containing Ba^{2+} is added to a solution containing CuY^{2-}?

(10 marks)

(d) Briefly explain the chemistry pertaining to the following statements.

(i) CrO_4^{2-} ion is used in the titrimetric determination of Ag^{+} ions with Cl^{-} ions.

(ii) $K_2Cr_2O_7$ is widely used in redox titrations.

(15 marks)

PART 'B'

1 B. Answer **all** parts

(a) Define briefly each of the following terms.

(i) End point

(ii) Equivalence point

(iii) Primary standard

(iv) Buffer solution

(20 marks)

(b) Consider the ethanoic acid (CH_3COOH) / sodium ethanoate ($CH_3COO^-Na^+$) buffer system.

(i) Giving equations where ever necessary, briefly explain how the above buffer system acts against small change in H^+ and OH^- ions.

(24 marks)

(ii) Calculate the pH of a buffer solution whose $[CH_3COOH]$ is 0.1 mol dm^{-3} and $[CH_3COO^-]$ is 0.1 mol dm^{-3}. The K_a of the weak acid CH_3COOH is 2×10^{-4} mol dm^{-3}.

(20 marks)

(c) Assume you are titrating 50.00 mL of 0.05 M HCl solution with 0.10 M NaOH.

(i) Calculate the pH at the following points.

(I) After addition of 10.00 mL 0.10 M NaOH solution.

(II) After addition of 25.00 mL 0.10 M NaOH solution.

(30 marks)

(ii) If the initial pH of the 0.05 M HCl solution is 1.30 and the pH of the mixture after addition of 25.10 mL of 0.10 M NaOH is 10.12, generate the hypothetical titration curve for the above titration.

(06 marks)

(02) Answer **all** parts

(a) Define the following terms.

(i) Precision
(ii) Accuracy
(iii) Absolute error

(15 marks)

(b) (i) Briefly explain how you would minimize systematic errors associated with analytical measurements.

(15 marks)

(ii) Suppose you have given a Cr containing alloy to determine % Cr in the sample. The sample was dissolved in dilute HCl and back titrated with EDTA. The results are shown in the following table. Report the Cr percentage in alloy at 95 % confidence level.

Sample	% Cr
1	0.0321
2	0.0320
3	0.0325
4	0.0319
Avg	0.0321
s	0.0003

(25 marks)

(c) A student used iodometric method to determine the iodide content in a commercial table salt sample and obtained the following data.

Titration #	Iodide content mg/kg
1	43
2	48
3	39
4	63

(i) Find the mean and standard deviation.

(ii) Calculate the coefficient of variation.

(iii) Identify if any rejectable data point at the 95% confidence level.

(45 marks)

Note : (i) Confidence limits are defined : $\mu = \bar{x} \pm \frac{ts}{\sqrt{N}}$ where μ is the sample mean and s is the standard deviation.

(ii) Qcrit = $(|Xq-Xn|/X_{highest}-X_{lowest})$ where Xq is the questionable result and Xn is the nearest neighbor of the questionable result.

(iii) Values of t for various levels of probability and Rejection quotient at different confidence limits are attached.

Values of t for Various Levels of Probability

Degrees of Freedom	80%	90%	95%	99%	99.9%
1	3.08	6.31	12.7	63.7	637
2	1.89	2.92	4.30	9.92	31.6
3	1.64	2.35	3.18	5.84	12.9
4	1.53	2.13	2.78	4.60	8.61
5	1.48	2.02	2.57	4.03	6.87
6	1.44	1.94	2.45	3.71	5.96
7	1.42	1.90	2.36	3.50	5.41
8	1.40	1.86	2.31	3.36	5.04
9	1.38	1.83	2.26	3.25	4.78
10	1.37	1.81	2.23	3.17	4.59
15	1.34	1.75	2.13	2.95	4.07
20	1.32	1.73	2.09	2.84	3.85
40	1.30	1.68	2.02	2.70	3.55
60	1.30	1.67	2.00	2.62	3.46
∞	1.28	1.64	1.96	2.58	3.29

Rejection Quotient, Q, at Different Confidence Limits[a]

No. of Observations	Confidence Level		
	Q_{90}	Q_{95}	Q_{99}
3	0.941	0.970	0.994
4	0.765	0.829	0.926
5	0.642	0.710	0.821
6	0.560	0.625	0.740
7	0.507	0.568	0.680
8	0.468	0.526	0.634
9	0.437	0.493	0.598
10	0.412	0.466	0.568
15	0.338	0.384	0.475
20	0.300	0.342	0.425
25	0.277	0.317	0.393
30	0.260	0.298	0.372

PART 'C'

Answer all questions under the PART 'C'

03) (i) Define the term ionic strength (μ) stating the relevant equation.

(10 marks)

(ii) What is the ionic strength of a 0.0002 M $La(IO_3)_3$ solution? Assume complete dissociation and no formation of $LaOH^{2+}$.

(20 marks)

(iii) What is the equation for activity coefficient (γ) of a compound?

(10 marks)

(iv) Give the Debye-Hückel Equation that gives the Activity Coefficients of Ions.

(20 marks)

(v) Calculate the activity coefficient of Hg_2^{2+} in a solution of 0.033 M $Hg_2(NO_3)_2$.
You are provided with the following data.

Ion	**Ion size (α, pm)**	**Ionic Strength (μ, M)**				
		0.001	*0.005*	*0.01*	*0.05*	*0.1*
Hg_2^{2+}, SO_4^{2-}	400	0.867	0.740	0.660	0.445	0.355

(40 marks)

04) (i) What do you mean by the rate law of a reaction?

(10 marks)

(ii) Obtain the integrated rate laws for a first order reaction and a second order reaction.

(30 marks)

(iii) The decomposition of NO_2 at 300°C is described by the equation and yields the following data. $NO_2\ (g) \rightarrow NO\ (g) + 1/2\ O_2\ (g)$

Time (*s*)	**$[NO_2]$, *M***
0.0	0.01000
50.0	0.00787
100.0	0.00649
200.0	0.00481
300.0	0.00380

Show that the reaction is second order.

(50 marks)

(iv) What is the rate constant for the reaction?

(10 marks)

PART 'D'

Answer all parts under the PART 'D'

05. Answer **all** parts

(a) Write short accounts on each of the following.

(i) Atomic orbital

(ii) Molecular orbital

(10 x 2 marks)

(b) What are the possible quantum numbers for an electron in the following electronic configurations can have?

(i) $3p^1$

(ii) $4f^1$?

(05 x 2 marks)

(c) Of the following pairs of molecules given in parenthesis, explain briefly which one would have the lowest;

(i) ionic radius (Ca^{2+} and Sc^{3+})

(ii) bond angle (ICl_2^- and ICl_4^-)

(iii) dipolemoment (NH_3 and BF_3)

(10 x 3 marks)

(d) Calculate the wavelength of electromagnetic radiation emitted when the electron in a hydrogen atom undergoes a transition from n=4 to n=2.

Note: Rydberg constant $1.09737 \times 10^7\ m^{-1}$ (15 marks)

(e) Explain the following parts using the suitable molecular orbital diagrams.

(i) The He_2^- ion exists and has a positive bond order.

(ii) The bond length between N and O atoms in the NO molecule is higher than that of the NO^+ ion.

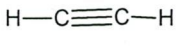
(25 marks)

PART 'E'

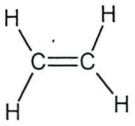
Answer all questions under PART 'E'

(06) Answer **all** parts

a) (i) Of the two compounds given below, which is more acidic? Using the concept of hybridization explain your answer.



Ethyne

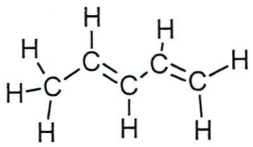


Ethene

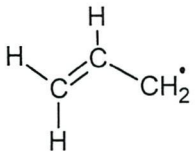
(ii) "BF_3 and $AlCl_3$ are categorized as Lewis acid". Explain this statement.

(16 marks)

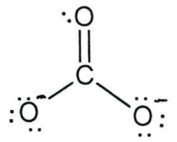
b) Consider the following molecules, free radicals and ions.



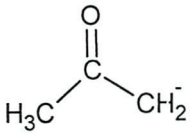
(I)



(II)



(III)



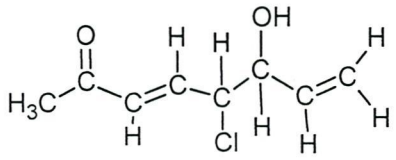
(IV)

(i) Draw the resonance structures for each molecules/ions.

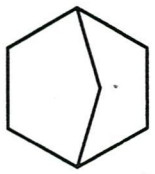
(ii) Of the resonance structures drawn for each, indicate their stability as more stable, less stable or equally stable etc. Give reasons for your answer in each case.

(30 marks)

(c) Name following compounds according to the IUPAC system of nomenclature.



(i)



(ii)

(08 marks)

d) Draw the structures of following molecules.

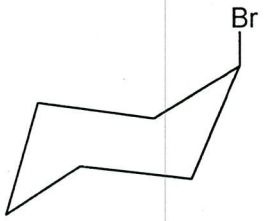
i) 2-formyl-4-oxocyclohexanecarboxylic acid
ii) Methyl 4-chloro-3-cyano-2-butenoate

(08 marks)

e)

(i) Briefly explain "Torsional strain" and "van der Waals strain"

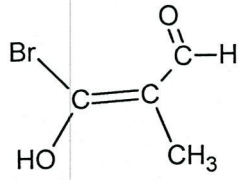
(ii) Consider the chair conformation of bromocyclohexane given below



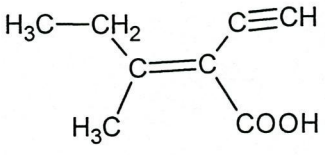
Draw the conformation formed after the ring flip of the above conformation. Of the two conformations, which one is the most stable? Explain your answer.

(18 marks)

f) Giving reasons, assign the configurations of following molecules as E or Z.



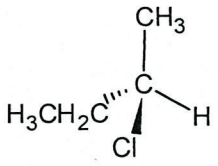
(i)



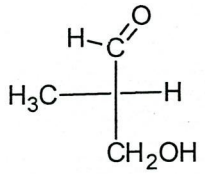
(ii)

(10 marks)

g) Giving reasons, assign the configurations of following molecules into R and S.



(iii)

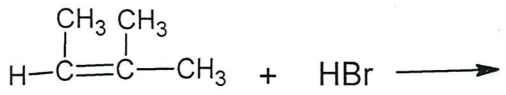


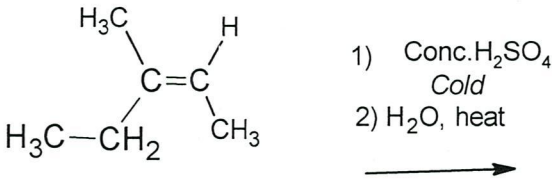
(iv)

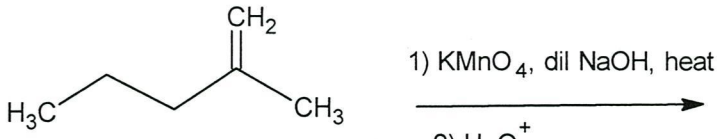
(10 marks)

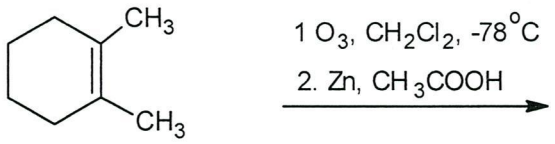
(07) Answer **all** parts

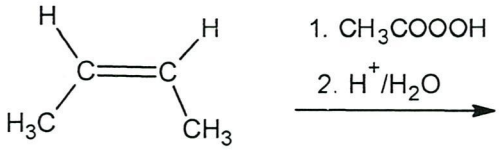
a) Draw the structures of the product(s) that would form in the reactions below. When more than one products are possible, indicate which is major and which is minor.

i) 

ii) 

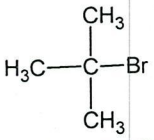
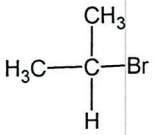
iii) 

iv) 

v) 

(40 marks)

b) Consider the following reaction and the data given in the table below.

R–Br	Relative rate
	1,200,000
	11.6
	1.05

(i) Name the type of the mechanism involved in the above reaction.
(ii) Propose a suitable mechanism for the reaction.
(iii) Based on the mechanism drawn, justify the relative rates given in the table

(20 marks)

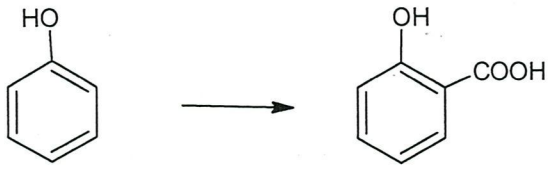
c)

(i) State the Huckel rule in aromaticity
(ii) Applying Huckel rule, show which molecule/ions given below are aromatic?

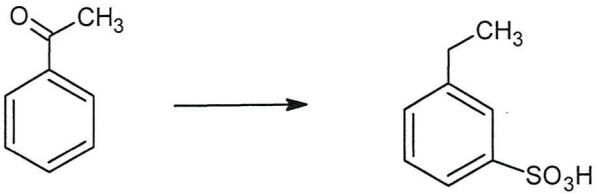
(16 marks)

d). Giving reagents and intermediate formed, show how you would carry out following conversions?

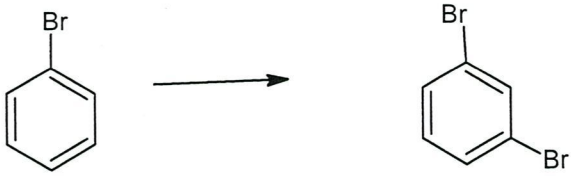
i)



ii)



iii)



(24 marks)

The Periodic Table of the Elements

	1												13	14	15	16	17	18
1	1 H Hydrogen 1.00794	2																2 He Helium 4.003
2	3 Li Lithium 6.941	4 Be Beryllium 9.012182											5 B Boron 10.811	6 C Carbon 12.0107	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.9984032	10 Ne Neon 20.1797
3	11 Na Sodium 22.989770	12 Mg Magnesium 24.3050	3	4	5	6	7	8	9	10	11	12	13 Al Aluminum 26.981538	14 Si Silicon 28.0855	15 P Phosphorus 30.973761	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948
4	19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955910	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938049	26 Fe Iron 55.845	27 Co Cobalt 58.933200	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge Germanium 72.61	33 As Arsenic 74.92160	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80
5	37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.29
6	55 Cs Cesium 132.90545	56 Ba Barium 137.327	57 La Lanthanum 138.9055	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.078	79 Au Gold 196.96655	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98038	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
7	87 Fr Francium (223)	88 Ra Radium (226)	89 Ac Actinium (227)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (263)	-107 Bh Bohrium (262)	108 Hs Hassium (265)	109 Mt Meitnerium (266)	110 (269)	111 (272)	112 (277)	113	114				

Lanthanide series	58 Ce Cerium 140.116	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92534	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93032	68 Er Erbium 167.26	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
Actinide series	90 Th Thorium 232.0381	91 Pa Protactinium 231.03588	92 U Uranium 238.0289	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

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