

UNIVERSITY OF RUHUNA

BACHELOR OF SCIENCE GENERAL DEGREE LEVEL II (SEMESTER I)
REPEAT EXAMINATIONS- JANUARY 2022

SUBJECT: Chemistry

COURSE UNIT: CHE 2114

TIME: **Three (03) hours**

Answer only **six (6)** questions by selecting **two (2)** from each of the sections, **A, B, and C**

Velocity of light, c	=	$3 \times 10^8 \text{ m s}^{-1}$
Avogadro's number, N_A	=	$6.022 \times 10^{23} \text{ mol}^{-1}$
Universal gas constant, R	=	$8.314 \text{ J}\cdot\text{K}^{-1} \text{ mol}^{-1}$
	=	$0.08021 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$
Boltzmann constant, k	=	$1.381 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$
Faraday constant, F	=	$9.6485 \times 10^4 \text{ C mol}^{-1}$
Electron charge, e	=	$-1.602 \times 10^{-19} \text{ C}$
Planck's constant, h	=	$6.626 \times 10^{-34} \text{ J}\cdot\text{s}$
Proton mass, m_p	=	$1.673 \times 10^{-27} \text{ kg}$
Electron mass, m_e	=	$9.10 \times 10^{-31} \text{ kg}$
Atomic mass unit, amu	=	$1.6606 \times 10^{-27} \text{ kg}$
Vacuum permittivity, ϵ_0	=	$8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$

Important conversion factors

$$1 \text{ atm} = 760 \text{ mmHg} = 1.01325 \text{ bar} = 101325 \text{ Pa}$$

$$2.303 (RT/F) = 59.15 \text{ mV at } 298.15 \text{ K}$$

$$1 \text{ eV} = 1.6022 \times 10^{-19} \text{ J}$$

1. Answer **all** parts.

(a) Define the following terms.

- (i) Ambidentate ligand
- (ii) Bidentate ligand
- (iii) Heteroleptic complexes

(24 marks)

(b) Which members of the following pairs of complexes would have a larger Δ_0 value? Give reasons for your answers.

- (i) $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Rh}(\text{NH}_3)_6]^{3+}$
- (ii) $[\text{Cr}(\text{OH}_2)_6]^{2+}$ and $[\text{Cr}(\text{OH}_2)_6]^{3+}$
- (iii) $[\text{CrF}_6]^{3-}$ and $[\text{Cr}(\text{NH}_3)_6]^{3+}$

(24 marks)

(c) (i) Write a short account on chelate effect and factors affecting the stability of chelates.

(12 marks)

(ii) Draw the structures of the following ethylenediamine (en) complexes and identify whether they are optically active or not.

- (I) cis- and trans- isomers of $[\text{Co}(\text{en})_2\text{Cl}_2]$
- (II) Δ and Λ isomers of $[\text{Co}(\text{en})_3]^{3+}$

(20 marks)

(d) Magnetic properties of $[\text{PdBr}_4]^{2-}$ and $[\text{Pd}(\text{CN})_4]^{2-}$ show that $[\text{PdBr}_4]^{2-}$ is a paramagnetic complex with two unpaired electrons while $[\text{Pd}(\text{CN})_4]^{2-}$ is a diamagnetic complex.

- (i) Explain briefly the magnetic properties of the above two complexes using crystal field splitting energy diagrams.
- (ii) Draw the structure of each complex.

(20 marks)

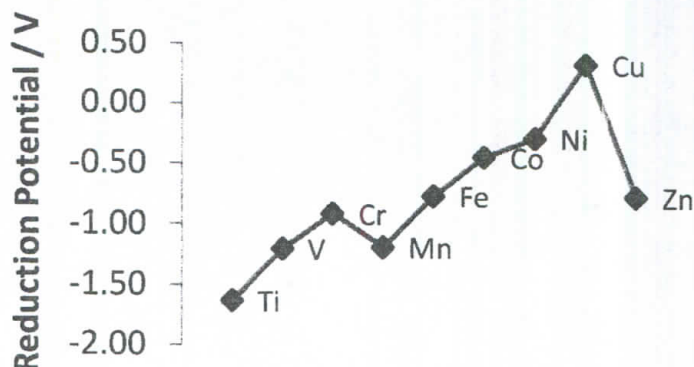
2. Answer **all** parts.

(a) (i) Give a brief comparative account on non transition metals and transition metals.

(ii) Explain why the enthalpy of atomization of zinc is the lowest in the series, Sc - Zn.

(30 marks)

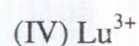
- (b) Variation of the standard reduction potentials for M^{2+}/M of the first transition metal series is shown in the following figure.



- (i) Explain this variation of the reduction potentials across the series. (10 marks)
- (ii) Justify why Mn and Zn deviate from the general trend. (20 marks)
- (iii) Predict the stability of Ti metal in water. (10 marks)
- (c) Use crystal field splitting diagrams to show the electron distribution of the two complexes $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Fe}(\text{CN})_6]^{4-}$. (10 marks)
- (d) Calculate the spin only magnetic moment of the complex $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$. (20 marks)

3. Answer **all** parts.

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



(20 marks)

- (ii) Which ion is more stable out of Eu^{3+} and Gd^{3+} ? Give the reasons for your answer.

(10 marks)

(iii) Monazite deposits are found in Induruwa and Polkatuwa area near Beruwala. Suggest a suitable procedure to obtain a crude basic salt of Th from monazite using the "acid opening" separation method.

(20 marks)

(b) Describe briefly each of the following.

- (i) Half life
- (ii) Nuclear binding energy
- (iii) Isotope dilution

(15 marks)

(c) Identify the elements/particles named as **A**, **B**, **C**, and **D** in each of the following nuclear equations. Identify the type of nuclear process in each case.



(20 marks)

(d) Ac-225 decays by successive emission of three α -particles. Write the balanced nuclear equations for these decay processes.

(15 marks)

4. Answer **all** parts.

(a) Ethylenediaminetetraacetic acid (EDTA) is the most widely used complexing agent in complexometric titrations.

(i) Give the chemical structure of EDTA and indicate its ligating sites.

(10 marks)

(ii) What are the five types of titration methods used in EDTA titrations?

(15 marks)

(iii) Write the balanced chemical equations for the reactions of M^{2+} and M^{3+} metal ions with the sodium salt of EDTA ($\text{Na}_2\text{H}_2\text{Y}$).

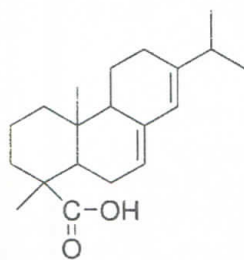
(10 marks)

- (b) In complexometric titrimetry, Ni^{2+} can be analyzed by a back titration using a standard Zn^{2+} solution at pH 5.5 with *xylene orange* as the indicator. A solution containing 25.00 mL of Ni^{2+} in dilute HCl was treated with 25.00 mL of 0.0528 mol L⁻¹ EDTA solution. The solution was neutralized with NaOH and the pH was adjusted to 5.5 with acetate buffer. The solution turned yellow when added a few drops of indicator. Then titration with 0.0229 mol L⁻¹ Zn^{2+} solution required 17.61 mL to reach the red end point. Calculate the concentration of Ni^{2+} in the unknown solution. (20 marks)
- (c) Explain briefly the following analytical methods used in argentometric titrations.
 (i) Volhard method
 (ii) Mohr method (20 marks)
- (d) What is the standard addition method used in atomic absorption spectroscopy. Write down the steps you follow in standard addition method briefly. (25 marks)

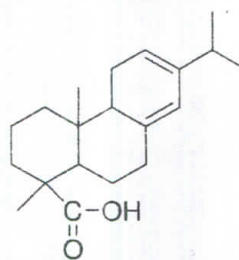
5. Answer **all** parts.

(a) The questions below are related to UV-visible spectroscopy.

- (i) Draw an energy level diagram to show the possible electronic transitions that can occur in UV-visible spectroscopy. Indicate the relevant transitions in the same diagram. (20 marks)
- (ii) Calculate the λ_{max} for the following molecules **A** and **B** using Woodward Fisher rules. (20 marks)



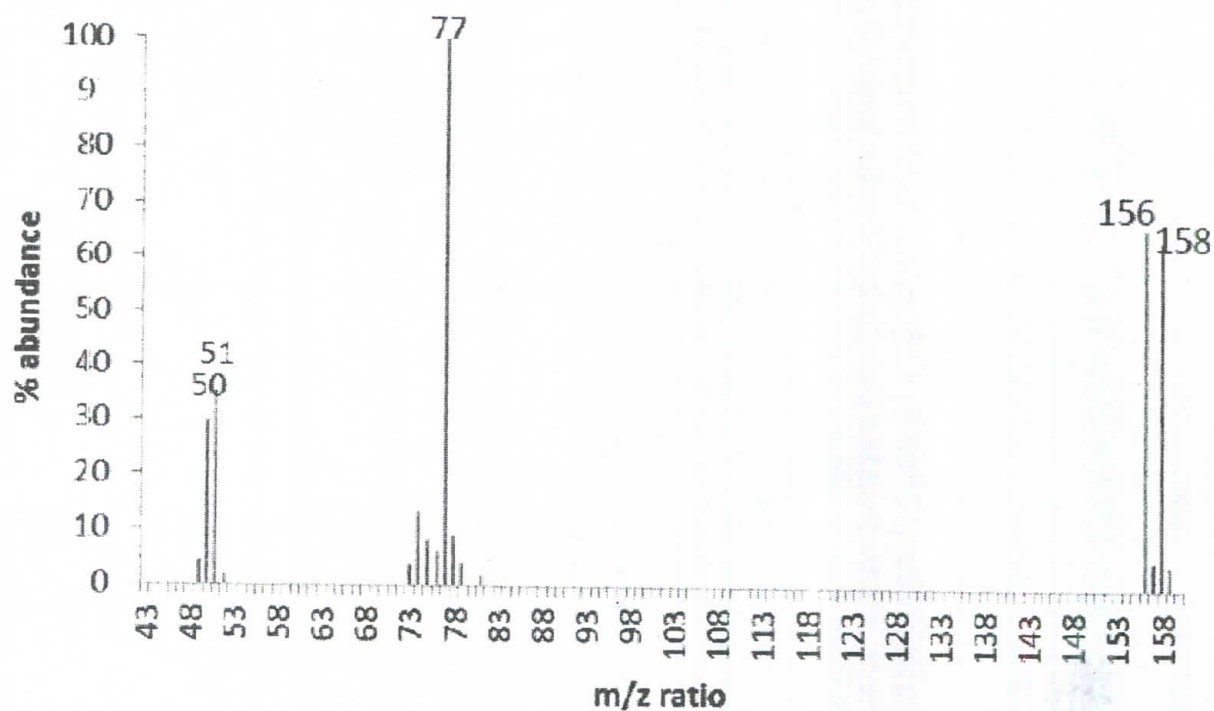
A



B

- (iii) Explain briefly why some organic molecules do not show an absorption band in UV-visible region. (10 marks)

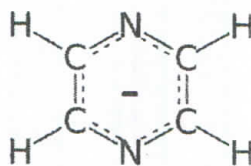
(b) The mass spectrum of an aromatic halide is given below. Answer the following questions based on the given spectrum.



- Giving reasons, identify the halogen atom.
- Draw the structure of the most likely molecular ion.
- Draw the structure of the ion responsible for the base peak.
- If there are two peaks at $m/z = 125.902$ and $m/z = 126.019$ in a mass spectrum, calculate the mass resolution required to resolve the two peaks above.

(26 marks)

(c) Draw the expected ESR spectrum of the following pyrazine anion. Clearly indicate the intensity ratios of each peak in your spectrum. (I values of N and H are 1 and $\frac{1}{2}$ respectively).



(24 marks)

6. Answer **all** parts.

(a) IR spectroscopy is widely used in structure determination of organic molecules.

(i) What are the two factors affecting stretching frequency in IR spectroscopy? Explain briefly explain how these two factors affect the stretching frequency.

(ii) Giving reasons, arrange the set of bonds given below in the increasing order of their stretching frequencies.

(I) $C\equiv N$, $C=C$, $C-H$

(II) $C=O$ of $C_2H_5COCH_3$, C_2H_5COCl , and C_2H_5COOH

(III) sp^3 hybridized $C-H$, sp^2 hybridized $C-H$ and sp hybridized $C-H$

(30 marks)

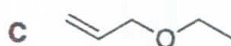
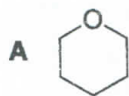
(b) Assign each set of IR absorption bands given below (i-iv) to the corresponding isomers (**A**, **B**, **C**, and **D**) of $C_5H_{10}O$ and indicate the absorption bands specific to the relevant bond vibrations.

(i) 1660 cm^{-1} , 1100 cm^{-1}

(ii) 3400 cm^{-1} , 1660 cm^{-1}

(iii) 1715 cm^{-1}

(iv) 1100 cm^{-1}



(20 marks)

(c) 1H NMR spectroscopy is a tool which can use in the identification of organic molecules. Answer the following questions pertaining to NMR spectroscopy

(i) Describe briefly the following terms.

(I) chemical shift

(II) spin-spin coupling

(12 marks)

(ii) Predict the number of peaks and their multiplicity that you would expect in the 1H NMR spectra of the following molecules.

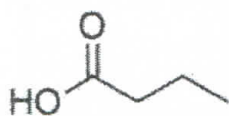
(I) 3-pentanone

(II) 1-bromo-2-chloropropane

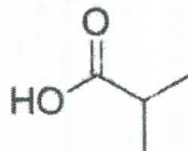
(III) 4-chlorophenol

(18 marks)

- (iii) Given below are the structures of isomers of butyric acid and isobutyric acid with the chemical formula of $C_4H_8O_2$. If you are provided the 1H NMR spectra of these two molecules, explain how you would distinguish these two isomers using the given spectra? Give the multiplicity of each peak.



Butyric Acid



Isobutyric Acid

(20 marks)

7. Answer **all** parts.

- (a) (i) List the basic symmetry elements with their standard symbols.

(ii) Using $PtCl_4^{2-}$ complex, describe the relevant symmetry operations associated with the above symmetry elements listed in (i)

(35 marks)

- (b) Use the BCl_3 molecule to sketch the following symmetry elements.

- (i) Principal rotational axis.
- (ii) Horizontal mirror plane.
- (iii) Vertical mirror plane.

(15 marks)

- (c) Giving major symmetry elements, assign the following molecules into their point groups.

- (i) H_2O
- (ii) NH_3
- (iii) CO_2
- (iv) benzene

(38 marks)

- (d) Using the answer to the Part (c) above, predict the polarity of the molecules given in Part (c).

(12 marks)

8. Answer all parts.

- (a) Rotations in a diatomic molecule can be approximated as a rigid linear rotor, whose energy (E_J) is given by

$$E_J = \frac{\hbar^2}{2I} J(J+1)$$

- (i) Show that the wavenumber ($\tilde{\nu}$) of the rotational absorption between adjacent states ($J+1 \leftarrow J$) in a linear rotor can be expressed as

$$\tilde{\nu} = 2\tilde{B}(J+1),$$

where \tilde{B} is defined as $\tilde{B} = \frac{\hbar}{4\pi cI}$

(20 marks)

- (ii) If the difference between the first two spectral lines in a pure rotational spectrum of hydrogen iodide ($^1\text{H}^{127}\text{I}$) is 13 cm^{-1} , calculate the rotational constant (\tilde{B}), moment of inertia perpendicular to the molecular axis (I), and bond length for the molecule within the rigid rotor approximation. The atomic masses of ^1H and ^{127}I are 1.01 amu and 126.90 amu, respectively, and $1 \text{ amu} = 1.661 \times 10^{-27} \text{ kg}$.

(40 marks)

- (b) A simple harmonic oscillator at small displacements is a reasonable model for diatomic vibrations and its energy can be given by

$$E_v = \hbar \left(\frac{k}{\mu} \right)^{\frac{1}{2}} \left(v + \frac{1}{2} \right)$$

Symbols have their usual meanings.

- (i) Show that the wavenumber ($\tilde{\nu}$) of the vibrational absorption between adjacent states ($v+1 \leftarrow v$) in a harmonic oscillator can be expressed as

$$\tilde{\nu} = \frac{1}{2\pi c} \left(\frac{k}{\mu} \right)^{\frac{1}{2}}$$

(25 marks)

- (ii) The infrared spectrum of $^1\text{H}^{127}\text{I}$ shows an intense transition at 2230 cm^{-1} . Calculate the force constant of the molecule within the simple harmonic oscillator model.

(15 marks)

9. Answer **all** parts.

(a) Below 912 °C, iron crystallizes into its α -iron allotrope, which has a body-centred cubic crystal structure. If the edge length of the unit cell (a) is 287 pm, calculate the density of iron. (The molar mass of Fe is 55.84 g.)

(15 marks)

(b) Find the Miller indices (hkl) of the planes that intersect the a, b and c axes at the distances $(a, b, c), (\infty a, b, 2c)$ and $(-a, b, \frac{1}{2}c)$.

(15 marks)

(c) When X-rays of wavelength 95 pm were reflected by the $\{211\}$ planes of a cubic crystal, the first-order reflection ($n = 1$) was observed at an angle of 15.8°. Using Bragg's law, calculate the lattice parameter a of the crystal.

(20 marks)

(d) (i) State the first law of photochemistry.

(10 marks)

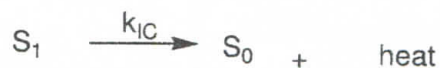
(ii) Briefly explain why an excited triplet state always has a lower energy than that of the corresponding excited singlet state.

(10 marks)

(iii) A solution of an inorganic complex in a 1.00 cm cell has an absorbance of 0.365. If the molar absorption coefficient is $1.11 \times 10^3 \text{ m}^2 \text{ mol}^{-1}$, calculate the concentration of the complex in mol m^{-3} .

(15 marks)

(iv) Consider the following reaction sequence for the deactivation process of the molecule at singlet excited state (S_1).



Derive an expression for the fluorescence quantum yield Φ_f

(15 marks)

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PERIODIC TABLE OF ELEMENTS

1	H	2	He
	Hydrogen Alkali		Helium Noble
3	Li	4	Be
	Lithium		Beryllium
11	Na	12	Mg
	Sodium		Magnesium
19	K	20	Ca
	Potassium		Calcium
37	Rb	38	Sr
	Rubidium		Strontium
55	Cs	56	Ba
	Cesium		Barium
87	Fr	88	Ra
	Francium		Radium
21	Sc	22	Ti
	Scandium		Titanium
39	Y	40	Zr
	Yttrium		Zirconium
57	La	72	Hf
	Lanthanum		Hafnium
89	Ac	104	Rf
	Actinium		Rutherfordium
23	V	24	Cr
	Vanadium		Chromium
41	Nb	42	Mo
	Niobium		Molybdenum
59	Zr	60	Ni
	Zirconium		Nickel
73	Ta	74	W
	Tantalum		Tungsten
105	Db	106	Sg
	Dubnium		Seaborgium
25	Mn	26	Fe
	Manganese		Iron
43	Tc	44	Ru
	Technetium		Ruthenium
75	Re	76	Os
	Rhenium		Osmium
107	Bh	108	HS
	Bohrium		Hassium
27	Co	28	Ni
	Cobalt		Nickel
45	Rh	46	Pd
	Rhodium		Palladium
77	Ir	78	Pt
	Iridium		Platinum
109	Mt	110	Ds
	Meitnerium		Darmstadtium
29	Cu	30	Zn
	Copper		Zinc
47	Ag	48	Cd
	Silver		Cadmium
79	Au	80	Hg
	Gold		Mercury
111	Rg	112	Cn
	Roentgenium		Copernicium
31	Al	32	Ge
	Aluminum		Germanium
49	In	50	Sn
	Indium		Tin
81	Tl	82	Pb
	Thallium		Lead
113	Nh	114	Fl
	Nihonium		Flerovium
33	P	34	S
	Phosphorus		Sulfur
51	Sb	52	Te
	Antimony		Tellurium
83	Bi	84	Po
	Bismuth		Polonium
115	Mc	116	Lv
	Moscovium		Livermorium
35	Br	36	Kr
	Bromine		Krypton
53	I	54	Xe
	Iodine		Xenon
85	At	86	Rn
	Astatine		Radon
117	Ts	118	Og
	Tennessine		Oganesson

58	Ce	59	Pr	60	Nd	61	Pm	62	Sm	63	Eu	64	Gd	65	Tb	66	Dy	67	Ho	68	Er	69	Tm	70	Yb	71	Lu
	Cerium		Praseodymium		Neodymium		Promethium		Samarium		Europium		Gadolinium		Terbium		Dysprosium		Holmium		Erbium		Thulium		Ytterbium		Lutetium
90	Th	91	Pa	92	U	93	Np	94	Pu	95	Am	96	Cm	97	Bk	98	Cf	99	Es	100	Fm	101	Md	102	No	103	Lr
	Thorium		Protactinium		Uranium		Neptunium		Plutonium		Americium		Curium		Berkelium		Californium		Einsteinium		Fermium		Mendelevium		Nobelium		Lawrencium