

UNIVERSITY OF RUHUNA

BACHELOR OF SCIENCE GENERAL DEGREE LEVEL III (SEMESTER I)

REPEAT EXAMINATION – JULY 2023

SUBJECT : CHEMISTRY

COURSE UNIT : CHE 3114 (Repeat)

TIME : Three (03) hours

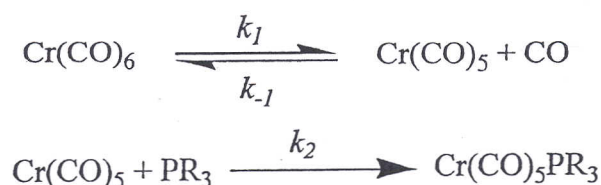
Answer six (06) questions only by selecting two (02) from Section A, one (01) from Section B and three (03) from Section C.

Velocity of light, (c)	$= 2.997 \times 10^8 \text{ m s}^{-1}$
Avagadro's number, (N_A)	$= 6.022 \times 10^{23} \text{ mol}^{-1}$
Universal Gas Constant, (R)	$= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Boltzmann constant, (k_B)	$= 1.381 \times 10^{-23} \text{ J K}^{-1}$
Faraday constant, (F)	$= 9.6485 \times 10^4 \text{ C mol}^{-1}$
Plank's constant, (h)	$= 6.626 \times 10^{-34} \text{ J s}$
Electron Charge, (e)	$= 1.602 \times 10^{-19} \text{ C}$
Proton mass, (m_p)	$= 1.673 \times 10^{-27} \text{ kg}$
Electron mass, (m_e)	$= 9.10 \times 10^{-31} \text{ kg}$
1 amu	$= 1.661 \times 10^{-27} \text{ kg}$
1 eV	$= 1.602 \times 10^{-19} \text{ J}$

Section - A

1. Answer **all** parts.

- (a) Substitution of CO by PR_3 in $\text{Cr}(\text{CO})_6$ is known to proceed *via* a dissociative mechanism as shown below.



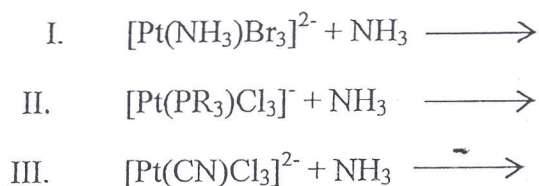
- (i) List **four (04)** characteristic features of a dissociative mechanism.

(20 marks)

- (ii) Using the steady-state approximation for the intermediate present, derive the rate law for the above dissociative reaction.

(40 marks)

(b) Consider the following three reactions.



(i) Predict the products of each reaction. Indicate clearly whether the formed products are *cis* or *trans*

(40 marks)

02. Answer all parts.

(a) Molar extinction coefficient coefficients (ϵ) of four transition metal complexes are given in the table below.

Complex	$\epsilon / \text{L mol}^{-1} \text{cm}^{-1}$
$[\text{TiCl}_6]^{2-}$	10,000
$[\text{CoCl}_4]^{2-}$	500
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	8-10
$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	0.02

(i) Explain briefly the selection rules which are governed the intensity of an absorption band of a transition metal complex.

(20 marks)

(ii) Giving reasons explain the variations of molar extinction coefficients of above complexes.

(20 marks)

(b) The electronic absorption spectrum of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ shows a band with a shoulder.

(i) Giving a suitable formula, derive the number of micro states for the metal ion of above complex.

(10 marks)

(ii) Derive possible term symbol(s) for the above transition metal complex.

(10 marks)

(iii) Sketch the electronic spectrum of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ using the appropriate correlation diagram.

- (iv) Explain the degeneracy of Mulliken symbols of the above correlation diagram with the aid of suitable diagrams. (20 marks)

(20 marks)

3. Answer **all** parts

- (a) An ore is usually concentrated by separating the desired mineral from waste materials before being refined into the pure metal.

- (i) Froth flotation is a very useful technique for carrying out such a separation. Briefly discuss the froth flotation method. (22 marks)

- (ii) Show (using a flow chart) how you expect to separate rutile (TiO_2) from a mixture of TiO_2 , PbS , SiO_2 and clay. (28 marks)

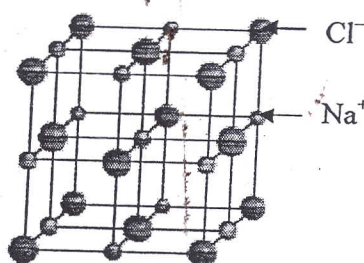
- (b) Define the following terms about the structure of crystalline solids.

(i) Unit cell

(ii) Coordination number

(10 marks)

- (c) A unit cell of the sodium chloride structure is shown below. The unit cell is cubic, and the structure can be viewed as a cubic close-packed array of Cl^- ions with Na^+ ions filling all the octahedral holes.



- (i) What is the coordination number of sodium and chloride ions in the structure above? (06 marks)
- (ii) How many sodium and chloride ions are in each NaCl unit cell? (10 marks)
- (iii) The density of NaCl is 2.17 g cm^{-3} . What is the side length of the NaCl unit cell? (Molar mass of NaCl is 58.44 g) (16 marks)
- (iv) What type of intrinsic point defect (Schottky or Frenkel) is most likely to find in NaCl? Justify your answer. (08 marks)

Section - B

04. Answer all parts

(a)

- (i) State four applications of Natural Products
- (ii) List out four solvent extraction methods applied in Natural Product extraction
- (iii) Explain following two term related to natural Product extraction
 - I. Isocratic extraction
 - II. Gradient Extraction

(40 marks)

(b)

- (i) Many new medicinal drugs are discovered in Natural product research. Sketch the method used in bio-assay guided fractionation of drug discovery process in the Natural products research
- (ii) What is the simple chromatographic technique that can be used to analyze a natural product crude mixture in the laboratory?

(40 marks)

(c)

- (i) State the main structural feature of true alkaloids
- (ii) What is the precursor molecule(s) used in the biosynthesis of alkaloids in the plants?
- (iii) Give brief extraction method used in the extraction of alkaloid from alkaloid bearing plant

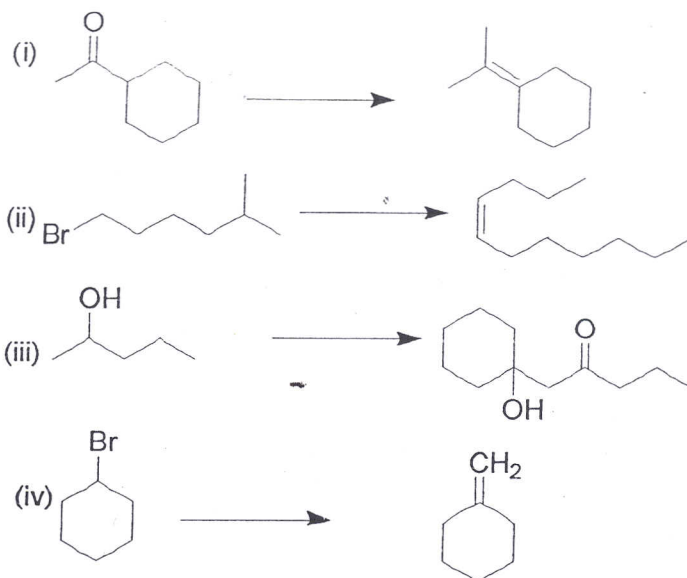
(20 marks)

05. Answer all parts

- (a) Carbocations are very useful reactive intermediates in organic synthesis. Discuss briefly the structure, stability and reactivity of carbocations.

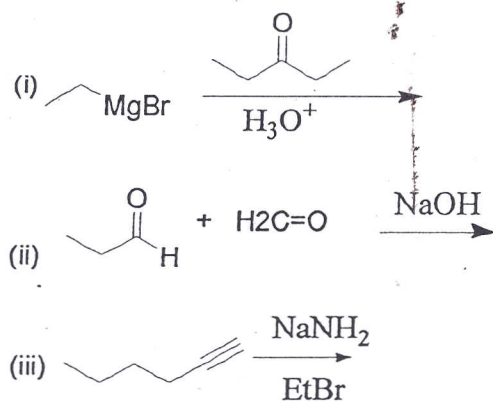
(22 marks)

- (c) Giving necessary reagents and reaction conditions show how you would carry out following conversions.



(48 marks)

(b) Give the major product(s) formed from the reactant(s) below under the given reaction conditions.



(30 marks)

Section - C

06. Answer all parts

(a) The surface tension arises due to cohesive interactions between the molecules in the liquid.

(i) Define surface tension and give its units (SI).

(20 marks)

(ii) When the radius of a cavity in equilibrium in a liquid with the surface tension γ , changes from r to $r+dr$, derive an expression for the force opposing stretching through an infinitesimal distance dr .

(20 marks)

(iii) Calculate the pressure differential of water across the surface of a spherical droplet of radius 300 nm at 20 °C. Note: γ_{water} at 20 °C is 72.75 mN m⁻¹.

(20 marks)

(iv) Mercury has an angle of contact equal to 140° with soda lime glass. A narrow tube of radius 2 mm, made of this glass is dipped in a trough containing mercury. By what amount does the mercury dip down in the tube relative to the liquid surface outside? Surface tension of mercury $\gamma = 0.456 \text{ N m}^{-1}$; Density of mercury $\rho = 13.6 \times 10^3 \text{ kg m}^{-3}$

(40 marks)

07. Answer all parts

(a) Concentration of unknown acetic acid solution determined by direct potentiometric method was not similar to the value obtained by potentiometric titration with standard NaOH solution.

(i) Comment on the above results.

(20 marks)

(ii) Write a critical account on potentiometric titration.

(20 marks)

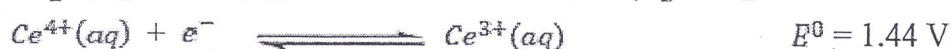
(b) Potentiometric titration with a standard Ce⁴⁺ solution can be used in the analysis of unknown U⁴⁺ solutions.

(i) Derive an expression to show that the electrode potential at the equivalence point is pH dependent.

(30 marks)

(ii) Determine the electrode potential at the equivalence point, if both solutions are prepared in H₂SO₄ solutions to maintain 0.100 M H⁺ concentration.

(30 marks)



18. Answer **all** parts

- (a) An electrochemical cell was constructed by connecting a Ag wire immersed in a AgNO_3 solution with a Cu wire immersed in a CuSO_4 solution. The solutions were connected with a salt bridge.

$$E^0 (\text{Ag}^+/\text{Ag}) = 0.80 \text{ V}, E^0 (\text{Cu}^{2+}/\text{Cu}) = 0.34 \text{ V}$$

- (i) Giving the reasons, Identify the anode and the cathode
- (ii) Write the standard cell notation for the above electrochemical cell
- (iii) Write the oxidation and reduction half-reactions
- (iv) Write the overall cell reaction -

(35 marks)

(b)

- (i) Discuss the quantitative and qualitative information that can be obtained from a voltammogram. (20 marks)
- (i) Discuss the reasons for observing current oscillations in polarogram. (20 marks)

(c)

- (i) Compare and contrast conventional volumetric titrations and coulometric titrations (25 marks)

19. Answer either Part X or Part Y

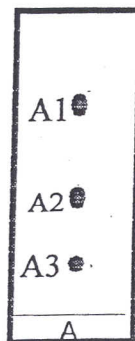
X. Answer **all** parts

- (a) Explain briefly the following terms related to Thin Layer Chromatography (TLC).

- (i) Stationary Phase
- (ii) Mobile phase
- (iii) Retention factor (R_f)

(30 marks)

- (b) The following diagram shows a chromatogram obtained from a TLC analysis to identify a food flavor.

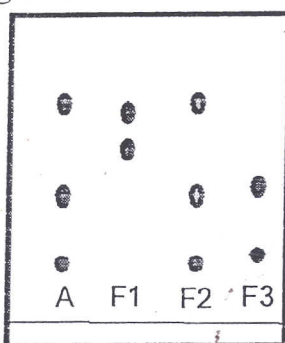


According to the diagram

- (i) How many components present in the food flavor?
(ii) Calculate the R_f values for the components if the solvent front is 7.0 cm and the distances from the base line are 1.1 cm, 2.9 cm, and 5.4 cm to the spots of A1, A2, and A3 respectively.

(36 marks)

- (c) In an experiment three food samples (F1, F2, and F3) were tested for the above food flavor in (b) and the following TLC result was obtained.



- (i) Indicate whether the food samples contain the food flavor?
(ii) Giving reasons identify which food sample contains the food flavor.

(34 marks)

Y. Answer all parts.

- (a) Explain the following facts.
(i) The fundamental properties of a solute that needs to consider to be used in solvent extraction.
(ii) The factors which determine the liquid-liquid extraction is the most suitable separation technique.
(iii) The disadvantage of "solvent extraction technique".

(55 marks)

- (b) In a solvent extraction 100 mL of a water immiscible organic solvent is shaken with 100 mL of aqueous solution containing 0.2 g of benzoic acid. The following data are given.

- The dissociation constant of benzoic acid $K_a = 6.5 \times 10^{-5}$ and
- The partition coefficient at equilibrium $K_p = 100$.

Calculate the distribution ratio D_c at pH = 2 and at 8.

N.B: Derive the necessary equations and use for this calculation.

(45 marks)

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