

**UNIVERSITY OF RUHUNA**

**BACHELOR OF SCIENCE GENERAL DEGREE (LEVEL II) SEMESTER II**

**EXAMINATIONS – JUNE 2022**

**SUBJECT: Chemistry**

**TIME: Two (02) hours**

**COURSE UNIT: CHE2222 (Physical and Analytical Chemistry)**

Answer **Four (04)** Questions Only

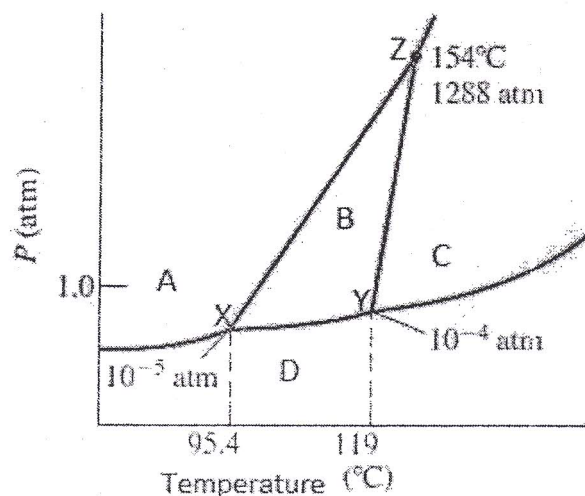
---

Avogadro's constant ( $N_A$ )	= $6.022 \times 10^{23} \text{ mol}^{-1}$
Atomic mass unit ( $amu$ )	= $1.6606 \times 10^{-27} \text{ kg}$
Boltzmann constant ( $k_B$ )	= $1.3806 \times 10^{-23} \text{ J K}^{-1}$
Electron charge ( $e$ )	= $-1.602 \times 10^{-19} \text{ C}$
Electron mass ( $m_e$ )	= $9.109 \times 10^{-31} \text{ kg}$
Faraday constant ( $F$ )	= $9.6485 \times 10^4 \text{ C mol}^{-1}$
Gas constant ( $R$ )	= $8.31446 \text{ J K}^{-1} \text{ mol}^{-1}$ = $0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$
Planck constant ( $h$ )	= $6.626 \times 10^{-34} \text{ J s}$
Proton mass ( $m_p$ )	= $1.673 \times 10^{-27} \text{ kg}$
Speed of light ( $c$ )	= $2.998 \times 10^8 \text{ m s}^{-1}$
Vacuum permittivity ( $\epsilon_0$ )	= $8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
1 eV	= $1.6022 \times 10^{-19} \text{ J}$

---

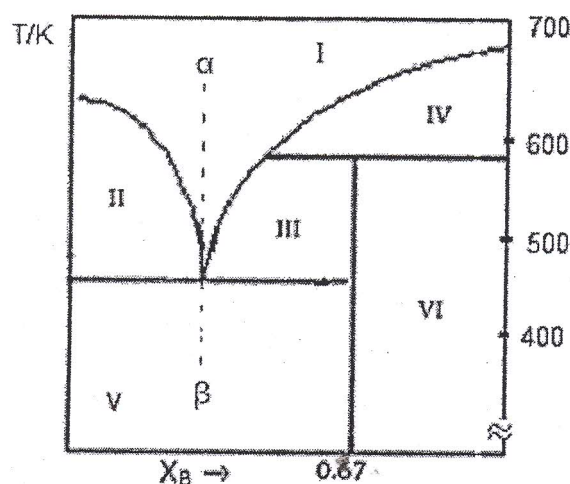
1. Answer all parts.

(a) Answer the following questions pertaining to the following phase diagram of sulphur.



- (i) What are the most important two allotropic forms of sulphur? (06 marks)
- (ii) Identify the phases in equilibrium with their physical states pertaining to the labeled areas A, B, C, and D. (12 marks)
- (iii) Name the existing phases of sulphur in equilibrium at triple points X, Y, and Z. (18 marks)

- (b) Phase diagrams of two-component systems illustrate significant features in behavior of binary mixtures. Using the following solid-liquid binary equilibrium phase diagram of A and B components, answer the following questions.



- (i) Define the eutectic composition. Write down the approximate eutectic composition of the system. Give the phases that exist in the eutectic mixture. (15 marks)
- (ii) Giving the formula of the compound formed, comment on the stability of the compound in the liquid state. (08 marks)
- (iii) Name the regions from I to VI with relevant phases in equilibrium. (08 marks)

**Note:** Use symbols  $S_A$  and  $L_A$  for solid A and liquid A, respectively and use a similar set of symbols for the other phases. Drawing of the diagram is not required.

- (iv) The melting points of pure components A and B, solid eutectic mixture, and the compound C are  $T_A$ ,  $T_B$ ,  $T_e$ , and  $T_C$ , respectively. Arrange them in the descending order. (24 marks)
- (v) Draw the cooling curve for the system cooling from point  $\alpha$  to point  $\beta$ . (08 marks)
- (09 marks)

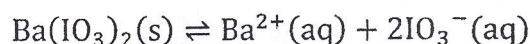


2. Answers all parts.

- (a) Solubility products may be determined from the conductivity measurements. The thermodynamic solubility product of a compound  $A_xB_y$  can be expressed by

$$K_{sp} = (a_{A^+})^x (a_{B^-})^y$$

For instance,  $a_{A^+} = \gamma_{A^+} m_{A^+}$ , where  $\gamma_{A^+}$  and  $m_{A^+}$  are the activity coefficient and molarity of the ion  $A^+$ , respectively. When an excess of barium iodate is dissolved in water, the following equilibrium is established:



The measured conductivity at 25 °C of the solution is  $9.91 \times 10^{-6} \text{ S cm}^{-1}$  while that for pure water is  $4.12 \times 10^{-8} \text{ S cm}^{-1}$ .

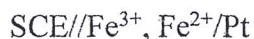
- (i) If the limiting molar conductivities of barium and iodate ions are  $127.3 \text{ S mol}^{-1} \text{ cm}^2$  and  $40.5 \text{ S mol}^{-1} \text{ cm}^2$ , respectively, indicating any assumption(s) you made, find the solubility of  $\text{Ba}(\text{IO}_3)_2$  at 25 °C. (20 marks)
- (ii) Calculate the activity coefficients for barium and iodate ions. *Hint*: approximate activity coefficients can be obtained from the Debye-Hückel limiting law. (20 marks)
- (iii) Calculate the activities for  $\text{Ba}^{2+}$  and  $\text{IO}_3^-$ , and hence determine the solubility product of  $\text{Ba}(\text{IO}_3)_2$  at 25 °C. (15 marks)
- (b) According to Bates and Bower (*Journal of Research of the National Bureau of Standards*, 53, 1954), the variation of the standard potential of the silver-silver chloride electrode ( $E^0$ ) with temperature ( $T$ ) is given by

$$E^0/V = 0.23659 - (4.8564 \times 10^{-4}) \left(\frac{T}{^\circ\text{C}}\right) - (3.4205 \times 10^{-6}) \left(\frac{T}{^\circ\text{C}}\right)^2 + (5.869 \times 10^{-9}) \left(\frac{T}{^\circ\text{C}}\right)^3$$

- (i) Find the temperature coefficient for the silver-silver chloride electrode at 25 °C. (15 marks)
- (ii) Consider the cell  $\text{Pt}(\text{s})|\text{H}_2(\text{g}, 1 \text{ atm})|\text{HCl}(\text{aq}, a_{\pm} = 1)|\text{AgCl}(\text{s})|\text{Ag}(\text{s})$ , for which the cell reaction is  $\frac{1}{2}\text{H}_2(\text{g}) + \text{AgCl}(\text{s}) \rightleftharpoons \text{HCl}(\text{aq}) + \text{Ag}(\text{s})$ . Using the above temperature coefficient, determine the standard enthalpy for the cell reaction at 25 °C. (30 marks)

3. Answer all parts.

- (a) Given below is a representation of an electrochemical cell with a titanium indicator electrode,

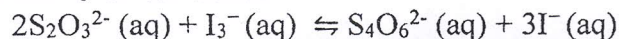


$$E(\text{SCE}) = 0.241 \text{ V}, E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = 0.771 \text{ V}$$

- If the concentrations of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  are  $0.0250 \text{ mol dm}^{-3}$  and  $0.0150 \text{ mol dm}^{-3}$ , respectively, calculate the cell potential ( $E_{\text{cell}}$ ) and the Gibbs free energy ( $\Delta G$ ) at  $25^\circ\text{C}$ .
- Write the standard electrode notation of SCE.
- Write down oxidation and reduction half reactions.
- Write the cell reaction for the spontaneous process.

(40 marks)

- (b) The purity of a  $\text{Na}_2\text{S}_2\text{O}_3$  sample was determined by a coulometric titration using KI as a mediator and  $\text{I}_3^-$  as the titrant.

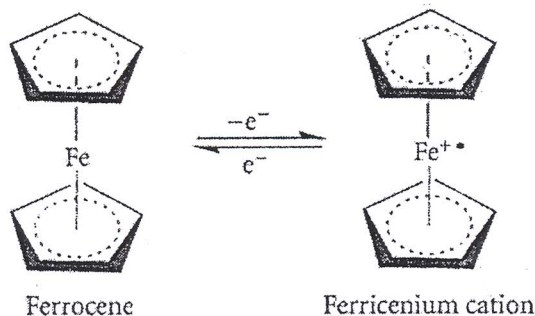


The sample weighing  $0.5000 \text{ g}$  was transferred to a  $100.00 \text{ mL}$  volumetric flask and diluted to the mark with distilled water. A  $10.00 \text{ mL}$  portion was transferred to an electrochemical cell and an indicator was added. Electrolysis was carried out at a constant current of  $40.34 \text{ mA}$  for  $245.1 \text{ s}$  to reach the endpoint.

- What is the purpose of adding a mediator?
- Name a suitable end point indicator.
- Calculate the purity of the sample as a percentage.

(35 marks)

- (c) A cyclic voltammetry experiment was carried out for the following reaction in an aqueous medium using a glassy carbon electrode with a surface area of  $0.07 \text{ cm}^2$ . The initial concentration of ferrocene was  $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ . The experiment was performed at a scan rate of  $100.0 \text{ mV/s}$ . Anodic and cathodic peak currents were  $20.15 \mu\text{A/cm}^2$  and  $20.46 \mu\text{A/cm}^2$ , respectively whereas anodic and cathodic peak potentials were  $293.5 \text{ mV}$  and  $219.5 \text{ mV}$ , respectively.



- Draw the expected cyclic voltammogram for the above experiment indicating all the details clearly.
- Calculate the diffusion coefficient for the reaction given that

$$I_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} \nu^{1/2} C$$

(25 marks)



4. Answer all parts.

Atomic absorption spectrophotometry (AAS) has been the most widely used method for nearly half a century for the determination of single elements in analytical samples.

- (a) List down **five** quantitative instrument performance criteria (Figures of Merits) that can be used to decide whether AAS method is suitable for attacking an analytical problem. (10 marks)
- (b) Illustrate the basic components of atomic absorption spectrophotometer using a labelled block diagram (20 marks)
- (c) Briefly explain the principle of AAS. (20 marks)
- (d) Describe how chemical interferences are occurred in AAS analysis. (10 marks)
- (e) The chromium concentration ( $C_x$ ) in an aqueous unknown sample ( $x$ ) was determined by pipetting 10.00 mL ( $V_x$ ) of the unknown into each of five 50.00 mL ( $V_t$ ) volumetric flasks. Various volumes ( $V_s$ ) of a standard ( $s$ ) containing 12.20 ppm ( $C_s$ ) Cr were added to the flasks, following which the solutions were diluted to the volume 50.00 mL. Samples were analyzed using AAS. The calibration curve was plotted using the following equation.

$$A = \frac{kC_s}{V_t} V_s + \frac{kV_x C_x}{V_t}$$

“A” is the instrument signal.  $C$  and  $V$  are the concentration and volume, respectively and  $k$  is a constant.

Standard Volume ( $V_s$ ), mL	Signal (A)
0.00	0.201
10.00	0.292
20.00	0.378
30.00	0.467
40.00	0.554

The calibration curve which was plotted using above data gives an equation of  $A = 0.0088 V_s + 0.2022$

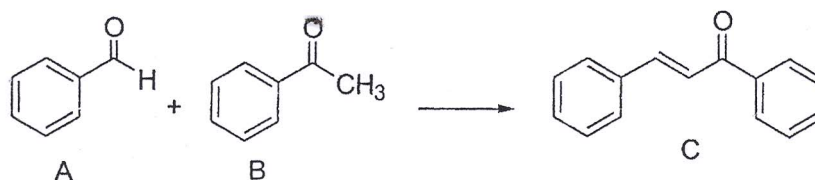
- (i) What is this calibration method called?
- (ii) What is the advantage of this calibration method compared to the other calibration methods?
- (iii) Determine the concentration of Cr in ppm in the unknown sample. (40 marks)

5. Answer all parts.

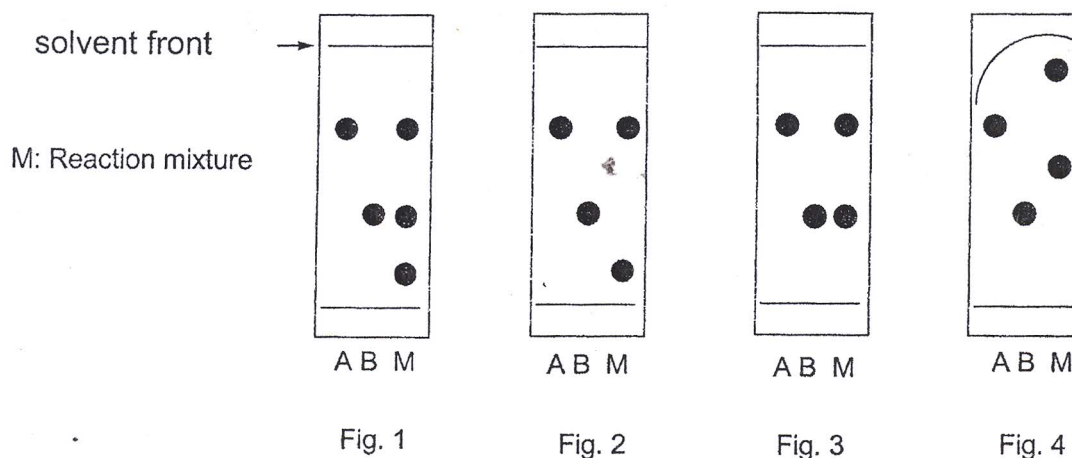
- (a) State **three** advantages of Thin Layer Chromatography (TLC) over other chromatographic techniques.

(18 marks)

- (b) The reaction of A and B produced only C as the product. Considering the reaction given below answer the questions (i) – (iv).



- (i) The following TLC observations (Fig. 1-4) were made in an experiment of monitoring the above reaction under identical experimental conditions (mobile phase is hexanes). Giving reasons assign the stages of the reaction (before the reaction starts, reaction in progress, reaction completed, erroneous experiment) for each of the TLC observations.

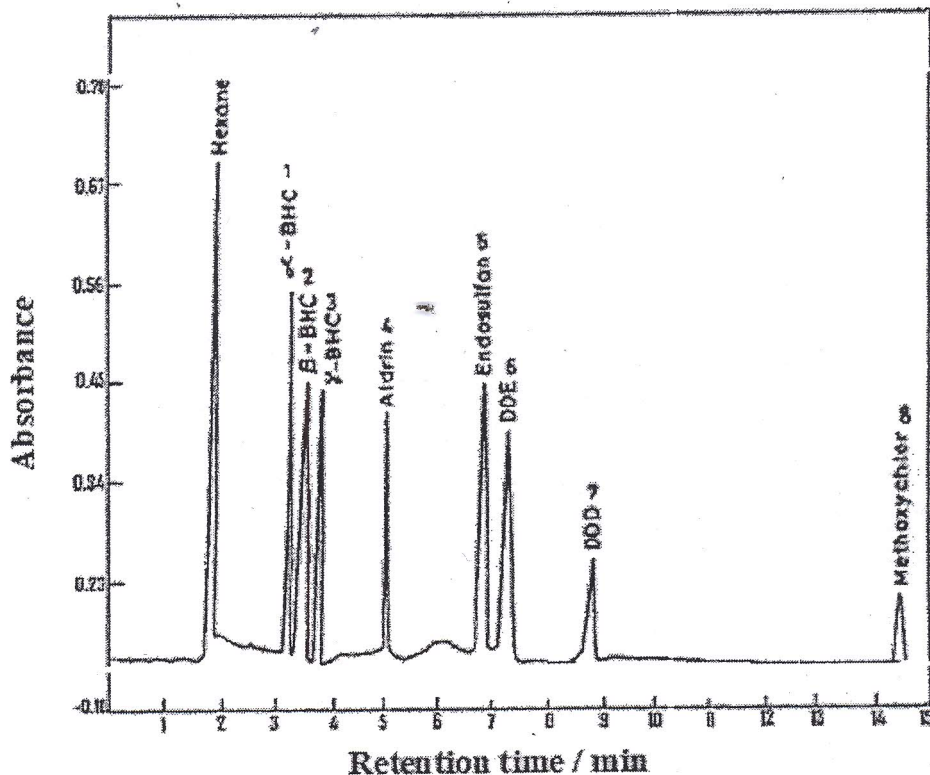


- (ii) In the Fig 1, if the distances from base line for the compounds A, B, C and solvent front are 2.0, 1.1, 0.4 and 2.8 cm respectively, determine the  $R_f$  values for the compounds A, B and C under these experimental conditions.
- (iii) Arrange the compounds A, B and C in the order of increasing their polarity.
- (iv) Write down the elution order of the components A, B and C if a mixture of A, B and C was subjected for a column chromatographic separation with the same experimental conditions used in above TLC experiments.

(42 marks)

- (c) A GC chromatogram obtained for a mixture of pesticides sample given below. The solvent peak relevant to hexane appears at 1.19 min.





- (i) What are the features of these pesticides that allow them to be suitable for gas chromatography (GC) analysis? (10 marks)
- (ii) How many pesticides are present in the sample according to the chromatogram shown above? (10 marks)
- (d) The distribution coefficient for a plant pigment in 1-octanol and water is given by

$$K_D = \frac{[X]_{\text{octanol}}}{[X]_{\text{water}}}$$

where [X] is the concentration of the component.

Calculate the volume of 1-octanol which is needed to extract 98% of the pigment to octanol from 50 mL of aqueous plant extract if  $K_D = 76$  for the above system.

(20 marks)

@@@@@@@@@@@@@@@@@@@@

# PERIODIC TABLE OF THE ELEMENTS

1 H 1.008 Hydrogen																	2 He 4.002602 Helium						
3 Li 6.94 Lithium	4 Be 9.0121831 Beryllium																	5 B 10.81 Boron	6 C 12.011 Carbon	7 N 14.007 Nitrogen	8 O 15.999 Oxygen	9 F 18.998403163 Fluorine	10 Ne 20.1797 Neon
11 Na 22.98976928 Sodium	12 Mg 24.305 Magnesium																	13 Al 26.9815385 Aluminium	14 Si 28.085 Silicon	15 P 30.973761998 Phosphorus	16 S 32.06 Sulfur	17 Cl 35.45 Chlorine	18 Ar 39.948 Argon
19 K 39.0983 Potassium	20 Ca 40.078 Calcium	21 Sc 44.955908 Scandium	22 Ti 47.867 Titanium	23 V 50.9415 Vanadium	24 Cr 51.9961 Chromium	25 Mn 54.938044 Manganese	26 Fe 55.845 Iron	27 Co 58.933194 Cobalt	28 Ni 58.6934 Nickel	29 Cu 63.546 Copper	30 Zn 65.38 Zinc	31 Ga 69.723 Gallium	32 Ge 72.630 Germanium	33 As 74.921595 Arsenic	34 Se 78.971 Selenium	35 Br 79.904 Bromine	36 Kr 83.796 Krypton						
37 Rb 85.4678 Rubidium	38 Sr 87.62 Strontium	39 Y 88.90584 Yttrium	40 Zr 91.224 Zirconium	41 Nb 92.90637 Niobium	42 Mo 95.94 Molybdenum	43 Tc 98 Technetium	44 Ru 101.07 Ruthenium	45 Rh 102.90550 Rhodium	46 Pd 106.42 Palladium	47 Ag 107.8682 Silver	48 Cd 112.414 Cadmium	49 In 114.818 Indium	50 Sn 118.710 Tin	51 Sb 121.760 Antimony	52 Te 127.60 Tellurium	53 I 126.90447 Iodine	54 Xe 131.293 Xenon						
55 Cs 132.90545196 Caesium	56 Ba 137.327 Barium	57 / 71	72 Hf 178.49 Hafnium	73 Ta 180.94788 Tantalum	74 W 183.84 Tungsten	75 Re 186.207 Rhenium	76 Os 193.22 Osmium	77 Ir 192.222 Iridium	78 Pt 195.084 Platinum	79 Au 196.966569 Gold	80 Hg 200.592 Mercury	81 Tl 204.38 Thallium	82 Pb 207.2 Lead	83 Bi 208.98040 Bismuth	84 Po 209 Polonium	85 At 210 Astatine	86 Rn 222 Radon						
87 Fr 223 Francium	88 Ra 226 Radium	89 / 103	104 Rf 261 Rutherfordium	105 Db 268 Dubnium	106 Sg 269 Seaborgium	107 Bh 270 Bohrium	108 Hs 278 Hassium	109 Mt 278 Meitnerium	110 Ds 281 Darmstadtium	111 Rg 281 Roentgenium	112 Cn 285 Copernicium	113 Uut 286 Ununtrium	114 Fl 289 Flerovium	115 Uup 289 Ununpentium	116 Lv 293 Livermorium	117 Uus 294 Ununseptium	118 Uuo 294 Oganesson						

Atomic Number → 1

Symbol → H

1.008 ← Atomic Mass

Hydrogen ← Name

Lanthanide Series

57 La 138.90547 Lanthanum	58 Ce 140.116 Cerium	59 Pr 140.90766 Praseodymium	60 Nd 144.242 Neodymium	61 Pm 145 Promethium	62 Sm 150.35 Samarium	63 Eu 151.964 Europium	64 Gd 157.25 Gadolinium	65 Tb 158.92535 Terbium	66 Dy 162.500 Dysprosium	67 Ho 164.93033 Holmium	68 Er 167.259 Erbium	69 Tm 168.93422 Thulium	70 Yb 173.054 Ytterbium	71 Lu 174.9668 Lutetium
------------------------------------	-------------------------------	---------------------------------------	----------------------------------	-------------------------------	--------------------------------	---------------------------------	----------------------------------	----------------------------------	-----------------------------------	----------------------------------	-------------------------------	----------------------------------	----------------------------------	----------------------------------

Actinide Series

89 Ac 227 Actinium	90 Th 232.0377 Thorium	91 Pa 231.03688 Protactinium	92 U 238.02891 Uranium	93 Np 237 Neptunium	94 Pu 244 Plutonium	95 Am 243 Americium	96 Cm 247 Curium	97 Bk 247 Berkelium	98 Cf 251 Californium	99 Es 252 Einsteinium	100 Fm 257 Fermium	101 Md 258 Mendelevium	102 No 259 Nobelium	103 Lr 260 Lawrencium
-----------------------------	---------------------------------	---------------------------------------	---------------------------------	------------------------------	------------------------------	------------------------------	---------------------------	------------------------------	--------------------------------	--------------------------------	-----------------------------	---------------------------------	------------------------------	--------------------------------