UNIVERSITY OF RUHUNA

BACHELOR OF SCIENCE GENERAL DEGREE (LEVEL II) SEMESTER II EXAMINATIONS – JUNE 2022

SUBJECT: Chemistry **TIME: Two (02) hours**

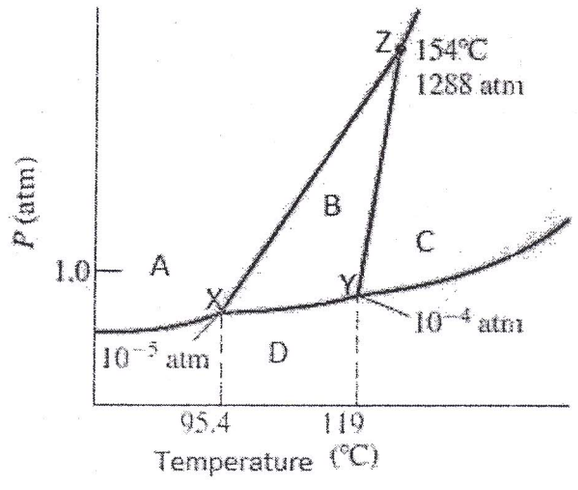
COURSE UNIT: CHE2222 (Physical and Analytical Chemistry)

Answer **Four (04)** Questions Only

Avogadro's constant (N_A)	= 6.022 x 10^{23} mol^{-1}
Atomic mass unit (amu)	= 1.6606 x 10^{-27} kg
Boltzmann constant (k_B)	= 1.3806 x 10^{-23} J K^{-1}
Electron charge (e)	= –1.602 x 10^{-19} C
Electron mass (m_e)	= 9.109 x 10^{-31} kg
Faraday constant (F)	= 9.6485 x 10^4 C mol^{-1}
Gas constant (R)	= 8.31446 J K^{-1} mol^{-1}
	= 0.08021 dm^3 atm K^{-1} mol^{-1}
Planck constant (h)	= 6.626 x 10^{-34} J s
Proton mass (m_p)	= 1.673 x 10^{-27} kg
Speed of light (c)	= 2.998 x 10^8 m s^{-1}
Vacuum permittivity (ε_0)	= 8.854 x 10^{-12} J^{-1} C^2 m^{-1}
1 eV	= 1.6022 x 10^{-19} 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 ma

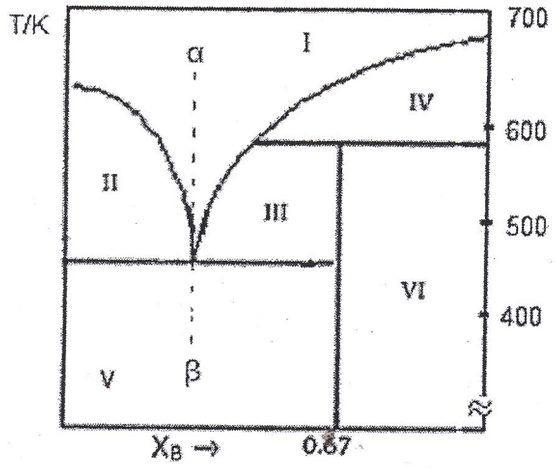
(ii) Identify the phases in equilibrium with their physical states pertaining to the labeled area A, B, C, and D.

(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 diagramme 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.

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.

(24 marks)

(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.

(08 marks)

(v) Draw the cooling curve for the system cooling from point α to point β.

(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 γ_{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:

$$Ba(IO_3)_2(s) \rightleftharpoons Ba^{2+}(aq) + 2IO_3^-(aq)$$

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

(i) If the limiting molar conductivities of barium and iodate ions are $127.3\, Smol^{-1}cm^2$ and $40.5\, Smol^{-1}cm^2$, respectively, indicating any assumption(s) you made, find the solubility of $Ba(IO_3)_2$ 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 Ba^{2+} and IO_3^-, and hence determine the solubility product of $Ba(IO_3)_2$ 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

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

(i) Find the temperature coefficient for the silver-silver chloride electrode at 25 °C.

(15 marks)

(ii) Consider the cell $Pt(s)|H_2(g, 1\ atm)|HCl(aq, a_{\pm} = 1)|AgCl(s)|Ag(s)$, for which the cell reaction is $\frac{1}{2}H_2(g) + AgCl(s) \rightleftharpoons HCl(aq) + Ag(s)$. 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,

$$SCE//Fe^{3+}, Fe^{2+}/Pt$$

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

(i) If the concentrations of Fe^{3+} and Fe^{2+} are 0.0250 mol dm^{-3} and 0.0150 mol dm^{-3}, respectively, calculate the cell potential (E_{cell}) and the Gibbs free energy (ΔG) at 25 °C.
(ii) Write the standard electrode notation of SCE.
(iii) Write down oxidation and reduction half reactions.
(iv) Write the cell reaction for the spontaneous process.

(40 marks)

(b) The purity of a $Na_2S_2O_3$ sample was determined by a coulometric titration using KI as a mediator and I_3^- as the titrant.

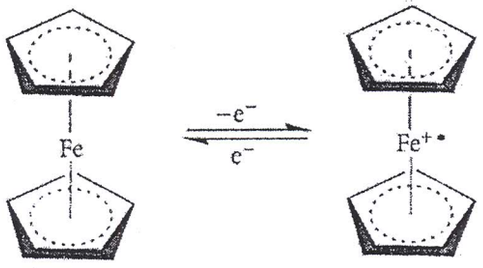
$$2S_2O_3^{2-}(aq) + I_3^-(aq) \leftrightharpoons S_4O_6^{2-}(aq) + 3I^-(aq)$$

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

(i) What is the purpose of adding a mediator?
(ii) Name a suitable end point indicator.
(iii) 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 cm^2. The initial concentration of ferrocene was 1.00×10^{-3} mol dm^{-3}. The experiment was performed at a scan rate of 100.0 mV/s. Anodic and cathodic peak currents were 20.15 $\mu A/cm^2$ and 20.46 $\mu A/cm^2$, respectively whereas anodic and cathodic peak potentials were 293.5 mV and 219.5 mV, respectively.



Ferrocene Ferricenium cation

(i) Draw the expected cyclic voltammogram for the above experiment indicating all the details clearly.
(ii) 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.

$$A = \frac{kC_s}{V_t}V_s + \frac{kV_xC_x}{V_t}$$

"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.

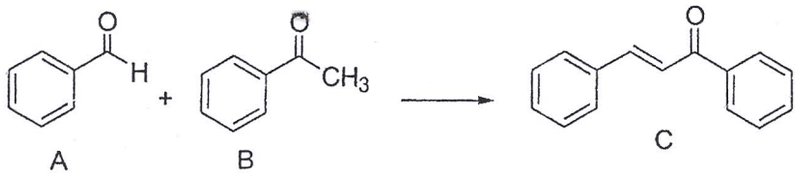
(40 marks)

5. Answer all parts.

(a) State **three** advantages of Thin Layer Chromatography (TLC) over other chromatographi 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.

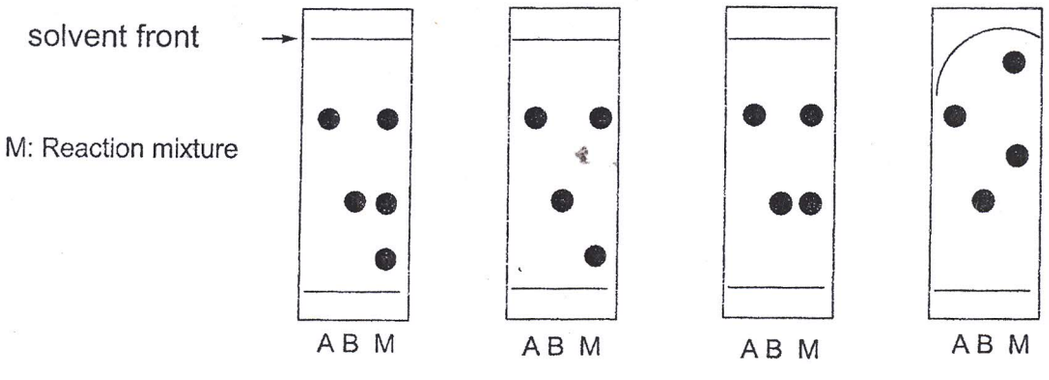


Fig. 1 Fig. 2 Fig. 3 Fig. 4

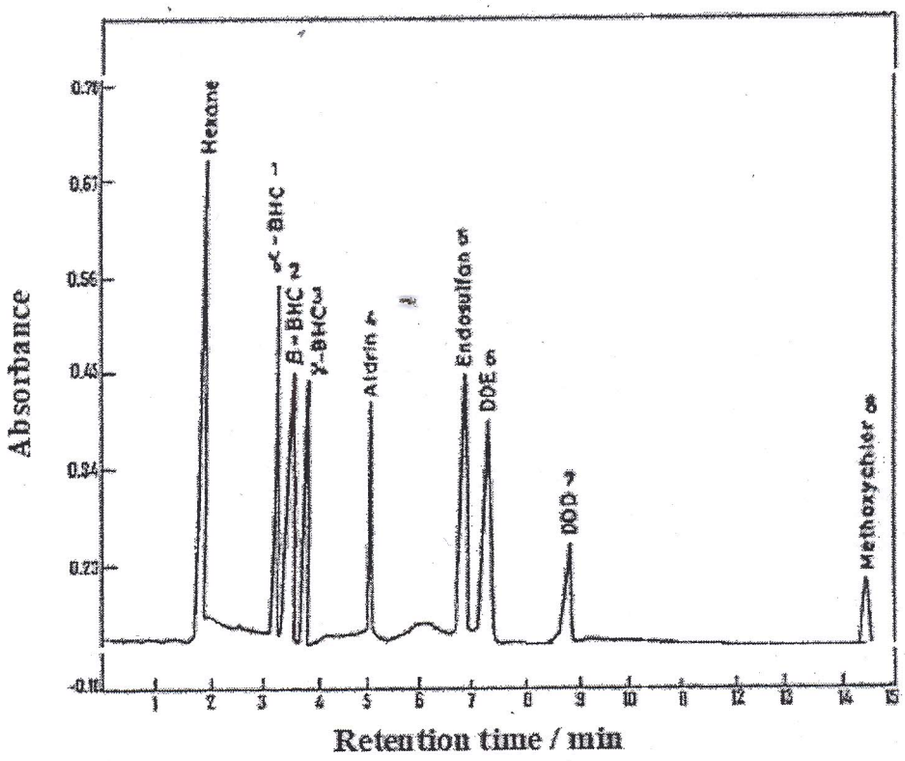
(ii) In the Fig 1, if the distances from base line for the compounds A, B, C and solvent front are 2.0, 1.1, 0.4 and 2.8 cm respectively, determine the R_f values for the compounds A, B and C under these experimental conditions.

(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

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

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