00847

The Open University of Sri Lanka
Faculty of Natural Sciences
B.Sc/B.Ed Degree Programme

Department	**: Chemistry**
Level	**: 4**
Name of the Examination	**: Final Examination**
Course Title and Code	**: CYU4301 – Concepts in Chemistry**
Academic Year	**: 2023/2024**
Date	**: 17.10.2023**
Time	**: 1.30 p.m. – 3.30 p.m.**
Duration	**: 2 hours**

General Instructions

1. Read all instructions carefully before answering the questions.
2. This question paper consists of **four (04)** questions in **eight (08)** pages.
3. Answer **all parts** of **all questions**. All questions carry equal marks.
4. Answer for each question should be started on a fresh page.
5. Answers to all parts of any question should be written together.
6. Draw fully labelled diagrams where necessary.
7. Involvement in any activity that is considered as an examination offense will lead to punishment.
8. Use blue or black ink to answer the questions.
9. Clearly state your index number on all pages of your answer script.
10. Use of non-programmable calculators will be allowed.
11. Mobile phones and other electronic equipment are not allowed. Switch off and leave them outside.
12. A list of constants and equations are provided overleaf for your reference.

Gas constant (R)	=	$8.314\ \mathrm{J\,K^{-1}\,mol^{-1}}$	
Avogadro constant (N_A)	=	$6.023\times10^{23}\ \mathrm{mol^{-1}}$	
Faraday constant (F)	=	$96{,}500\ \mathrm{C\,mol^{-1}}$	
Planck constant (h)	=	$6.63\times10^{-34}\ \mathrm{J\,s}$	
Velocity of light (c)	=	$3.0\times10^{8}\ \mathrm{m\,s^{-1}}$	
Standard pressure	=	$10^{5}\ \mathrm{Pa}\left(\mathrm{N\,m^{-2}}\right)$	= 1 bar
Protonic charge (e)	=	$1.602177\times10^{-19}\ \mathrm{C}$	
π	=	3.14159	
$\mathrm{Log}_e(X)$	=	$2.303\ \mathrm{Log}_{10}(X)$	

Some equations used in chemistry are given below using standard notation.

$\log(\gamma_\pm) = -A Z_+ |Z_-| \sqrt{I}$, $E_J = BJ(J+1)$, $\bar{B} = \dfrac{h}{8\pi^2 \mu R^2 c}$, $\bar{v} = 2\bar{B}(J+1)$,

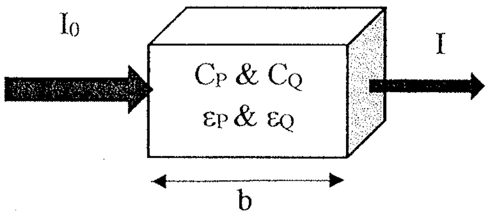
$\rho = \dfrac{I}{h v c}$, $u = \dfrac{x a \kappa}{Q}$, $\lambda_B = u_B |Z_B| F$, $v_B = u_B E$, $j = \kappa E$, $A = \varepsilon C l$,

$j_B = v_B c_B |Z_B| F$, $\Lambda_Y = \dfrac{\kappa_Y}{C_Y}$, $\lambda_B = \dfrac{\kappa_B}{c_B}$, $\kappa_B = u_B c_B |Z_B| F$.

(1). Answer **Part A (compulsory)**, and one of either **Part (B)** or **Part (C)** (but **NOT** both)

<u>Part A</u>

(a) Consider a sample containing two non-interacting chemical species (P & Q) both absorbs radiation and this radiation absorbing sample is schematically represented below,



Where, I_0 is the intensity of monochromatic radiation (frequency v) incident on the sample, I is the intensity of the radiation after travelling a distance b at 25 °C. C_P & C_Q are molar concentrations and ε_P & ε_Q are the molar absorption coefficients of P & Q respectively.

(i) Write down an equation to represent the Beer-Lambert law in terms of given symbols only.

(ii) A beam of monochromatic radiation of intensity 2.0 Wm^{-2} was passed through a sample of the above solution. The intensity of radiation emerging from the sample was 0.5 Wm^{-2}. Calculate the transmittance and the absorbance of the sample.

(iii) The ratio of concentrations of P and Q (C_P:C_Q) in the above solution is 1:3 while the concentration of P is 3 mol dm^{-3}, ε_P is 0.150 $mol^{-1}dm^3cm^{-1}$ and b is 1.0 cm. Based on the information provided, calculate the molar absorption coefficient of Q.

(iv) Sketch the graph of I versus path length at constant concentration.

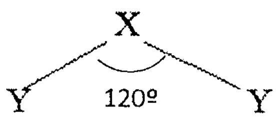
(50 marks)

Part B

(a) The bond angle of a molecule, AB_2, is 120° as depicted below. Atom Y is more electronegative than atom X. The dipole moment along each of the $\overrightarrow{XY}$ bond is 0.54 D.

(i) Calculate the dipole moment of XY_2 molecule.

(ii) Draw the molecule and indicate the net dipole moment vector.



(b)

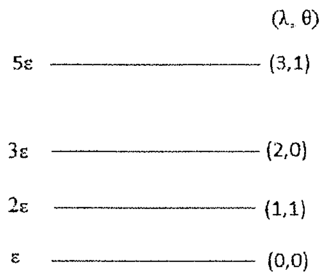
(i) Define the following terms.

(I) Stimulated absorption

(II) Stimulated emission

(ii) Consider a (hypothetical) gaseous molecule which has only four energy levels. If the populations of the two upper most levels of that molecule are zero at 25°C. Using a schematic representation of the energy level diagram, find out what is the maximum number of peaks observable in the absorption spectrum of this molecule at 25°C?

(iii) Consider a molecule having only four (4) energy levels with energies ε, 2ε, 3ε and 5ε. Each energy level is identified by two quantum numbers, (λ, θ) as shown in the figure to the right. The selection rules in absorption spectroscopy of the molecule is $\Delta\lambda = +1$ and $\Delta\theta = \pm 1$. The frequency of the highest frequency line in the absorption spectrum is 1.5×10^{13} Hz.



(I) What is the maximum number of lines that may be observed in the absorption spectrum of this molecule?

(II) What is the energy of the molecule in its ground state?

(50 marks)

Part C

(a) Briefly explain the following terms as applied in molecular spectroscopy.

(i) Bohr condition
(ii) Rotational energy
(iii) Component transition

(b)

(i) The energy components of four molecular energy levels, E_W, E_X, E_Y and E_Z, are (N2,e1,V5,R1), (N3,e1,V5,R1), (N3,e3,V5,R1) and (N3,e1,V6,R1) respectively. Denote the molecular energy transitions among these levels which involve pure nuclear, pure electronic and pure vibrational transitions. (N, e, v, and R are refer to nuclear, electronic, vibrational and rotational energy levels respectively).

(ii) What are the component transitions involved in the $E_W \rightarrow E_Z$ transition according to the energy components given above Q(b)(i)?

(iii) What are the changes in nuclear, electronic, vibrational, and rotational energies of the molecule in the transition, $E_W \rightarrow E_Z$?

(iv) In what region of the electromagnetic spectrum does the spectral feature/s produced by the transition $E_W \rightarrow E_Z$ most likely to appear? Briefly explain.

(50 marks)

(2). Let us imagine that a student uses the moving boundary method to determine the ionic mobility of P^{2+} using a 0.01 mol dm^{-3} solution of PCl_2. Next, he wanted to select a suitable solution for the ***following solution*** from the solutions of QCl_3, $P(NO_3)_2$, and RCl_2. The increasing order of ionic mobility and density is $Q^{3+} > P^{2+} > R^{2+}$. Then he selected the suitable solution and applied the moving boundary method by passing a current of 2.3 A for 30 minutes. The molar conductivities of 0.01 mol dm^{-3} PCl_2 solution and deionized water used to prepare the PCl_2 are 220 mS cm^2 mol^{-1} and 40 mS cm^2 mol^{-1} respectively.

(i) Express the molar conductivity of the strong electrolyte PCl_2 in terms of the molar conductivities of its ions. (Hint: $\Lambda_Y = \sum \left(\frac{c_B}{c_Y}\right) \lambda_B$)

(ii) Find the conductivity of PCl_2 in $S\ cm^{-1}$.

(iii) Identify the most suitable ***following solution*** by the three solutions given (QCl_3, $P(NO_3)_2$, and RCl_2). Justify your answer.

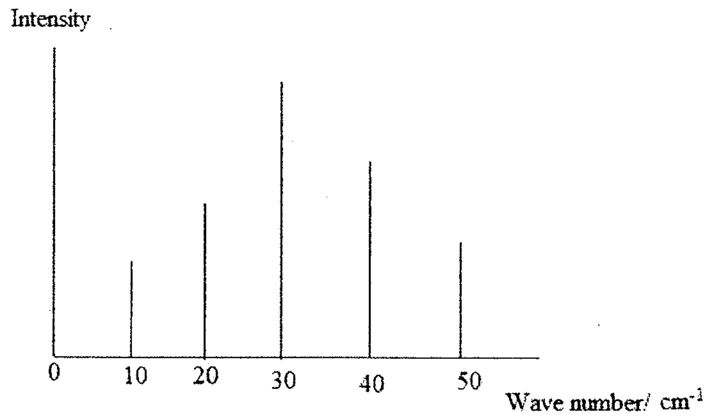
(iv) It was found that the distance moved by the boundary is 25 cm through the tube with the cross-sectional area of 0.5 cm^2. Determine the ionic mobility of the P^{2+} in $cm^2\ V^{-1} s^{-1}$.
(Hint: $U_{P^{2+}} = \frac{x a \kappa}{Q}$)

(v) If the ionic mobility of Cl^- in 0.01 mol dm^{-3} is $2.0 \times 10^{-9}\ cm^2\ V^{-1}\ s^{-1}$, find the transport number of the P^{2+}.

(vi) Briefly explain an experiment to determine the limiting molar conductivity of PCl_2 solution using a conductometer. (Hint: $\Lambda_Y = \Lambda_Y^0 - (a + b\Lambda_Y^0)\sqrt{\frac{c_Y}{c^0}}$)

(100 marks)

(3). (a) Positions of the first 5 transitions which involve the lowest frequency radiation, in the Microwave absorption spectrum of a diatomic molecule, AB, is schematically represented below.



(i) Starting with an equation that gives the position of lines in the Microwave spectrum of a diatomic molecule, deduce the relationship between the Rotational constant, B and the spacing between two adjacent lines in the microwave spectrum.
(ii) Deduce the value of the rotational constant of AB using the above figure.

(30 marks)

(b) (i) Write down the expression for the **Arrhenius equation** and clearly identify all the symbols used.

(ii) Consider a chemical reaction occurring at two different temperatures, T_1 and T_2, whose corresponding rate constants are k_1 and k_2, respectively. Show that the activation energy (E_a) of the reaction is given by the equation, $E_a = \frac{R\ ln\left(\frac{k_1}{k_2}\right)}{\left[\frac{1}{T_2} - \frac{1}{T_1}\right]}$. What is the major assumption that you made in deriving this equation?

(iii) The following experimental results were obtained for the first order reaction, $A \xrightarrow{k} B$ where k is the rate constant.

Rate/mol dm^{-3} s^{-1}	Concentration of A/mol dm^{-3}	Temperature/°C
0.100	1.00	27
0.200	1.00	37

(I) Write down the general rate equation (differential form) of this reaction using the standard symbols.
(II) Derive the units of rate constant.

(III) If the rate constants for this reaction are k_1 and k_2 at temperatures of 27 and 37 °C respectively, show that $\frac{k_1}{k_2} = \frac{1}{2}$.

(IV) Calculate the activation energy of this reaction.

(45 marks)

(c) (i) Define the term "**Steady State Approximation (SSA)** as applied in multi–step reaction mechanisms in chemical kinetics.

(ii) Consider the given first order consecutive reaction mechanism and answer the following questions.

$$\mathbf{A} \xrightarrow{\mathbf{k_1}} \mathbf{B} \xrightarrow{\mathbf{k_2}} \mathbf{C}$$

(I) Write down the expressions for $\frac{d[A]}{dt}$, $\frac{d[B]}{dt}$ and $\frac{d[c]}{dt}$.

(II) Derive the expressions using the rate constants, $[A_0]$ and time (t) for [A], $[B]_{steady\ state}$ and $[C]_{steady\ state}$, where $[A_0]$ is the initial concentration of A at time zero (t = 0).

(25 marks)

(4). (a) Explain the following terms

(i) Triple point of one component system
(ii) Degrees of freedom
(iii) An extensive variable

(15 marks)

(b) Sketch a clearly labeled phase diagram of one component system. Consider water as an example and illustrate the use of the Phase rule using this diagram.

(15 marks)

(c) 50.00 ml of a liquid P [relative molar mass 100 and density 800 kg m^{-3}] is mixed with 75.00 g of a liquid Q [relative molar mass = 125]. Assuming that this binary system is fully miscible, calculate the mole fraction of P in the solution.

(10 marks)

(d) Two liquids A and B are miscible for all compositions and form an ideal binary solution.

(i) Draw a fully labeled temperature (boiling point) *vs* composition (X_A) phase diagram to represent the above mixture at room temperature. Note that the vapor pressure of pure B is greater than that of pure A.

(15 marks)

(ii) A mixture, whose composition is given as X_A [mole fraction of A] = 0.8, is heated up to its boiling point, T_1. Mark this temperature on your sketch and, briefly outline (experimental details not necessary), how you would carry out fractional distillation of the above mixture in order to separate out A and B. (15 marks)

Answer either **Part (A)** **<u>OR</u>** **Part (B)** (But **<u>NOT</u>** Both)

Part A

(a) Define the following terms.
- (i) Azeotropic mixture
- (ii) Negative deviation from Raoults Law (in terms of forces between molecules)

(b) Ethanol and water, forms an azeotropic mixture with a minimum at 95.6% of ethanol by mass in the mixture. The boiling point of the azeotropic mixture is 78.2 °C, and the boiling point of pure ethanol is 78.5 °C.
- (i) Sketch the Boiling point vs Composition Phase diagram for ethanol-water system showing an azeotropic mixture at 95.6 % ethanol composition (by mass).
- (ii) Explain what would happen if you reboil the liquid of composition 95.6% ethanol?

(30 marks)

Part B

(a) Two metals A and B (melting point of B is greater than that of A) are said to form a simple eutectic system at elevated temperatures. The eutectic composition was found to be at $X_A = 0.40$ (X_A is the mole fraction of A).
- (i) Sketch a fully labeled phase diagram (Temperature verses mole fraction of B) for the above system.
- (ii) What do you understand by the term "eutectic composition"?

(b) The solubility curve of triethylamine and water shows a lower critical solution temperature (LCT). Sketch a fully labeled phase diagram (Temperature verses mole fraction of Triethylamine) for Triethylamine/water system.

(30 marks)

THE END