00713

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	**: 2024/2025**
Date	**: 05.12.2024**
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 on **eight (08)** pages.
3. Answer **required parts** of **all questions** as instructions given. 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 write 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 $J K^{-1} mol^{-1}$**
Avogadro constant (N_A)	=	**6.023×10^{23} mol^{-1}**
Faraday constant (F)	=	**96,500 $C\ mol^{-1}$**
Planck constant (h)	=	**6.63×10^{-34} J s**
Velocity of light (c)	=	**3.0×10^{8} $m\ s^{-1}$**
Standard pressure	=	**10^5 Pa$(N\ m^{-2})$ = 1 bar**
Protonic charge (e)	=	**1.602177×10^{-19} C**
π	=	**3.14159**
$Log_e(X)$	=	**2.303 $Log_{10}(X)$**

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

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

$\rho = \frac{1}{h\nu c}$, $u = \frac{x a \kappa}{Q}$ $\lambda_B = u_B|Z_B|F$, $v_B = u_B E$, $j = \kappa E$ $A = \varepsilon C l$,

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

1. Answer both **Part A** <u>**and**</u> **Part (B)** and one of either **Part (C)** <u>**or**</u> **Part (D)** (but **NOT** both)

Part A

(a) Consider a cell having a path length of 2.0 mm was filled with a solution of a dye dissolved in a non-absorbing solvent. The concentration of dye was 0.010 mol dm^{-3} and the wavelength of the radiation was 256 nm and at 25°C (where there is a maximum in absorption). Calculate the following.

(i) The absorbance of the dye solution at this wavelength, if the transmittance, T, was 48 percent (48%).
(ii) If the transmittance remains the same as (a)(i) above, calculate the molar absorption coefficient of the dye.
(iii) What will the transmittance be in a 4.0 mm cell at the same wavelength and temperature?

(b) Name three (03) conditions on which the molar absorption coefficient, (ε), of the above dye depends on.

(30 Marks)

Part B

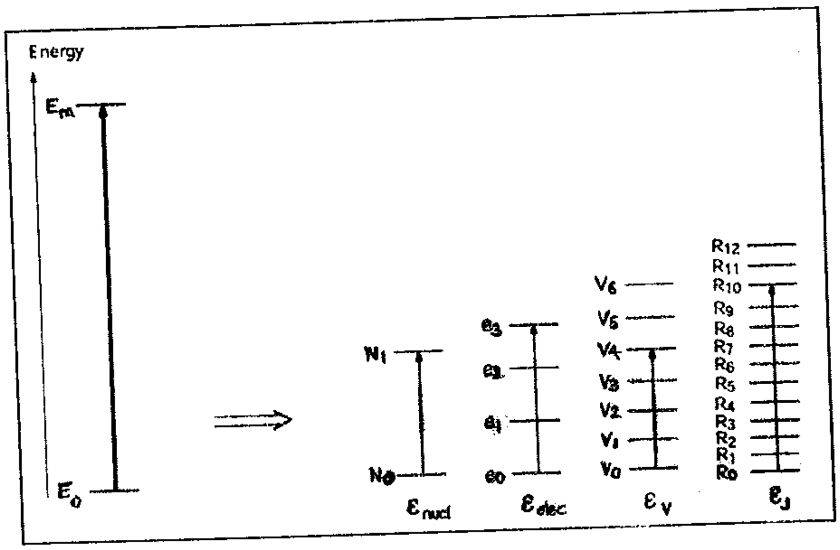
(a) Briefly explain the following terms relevant to molecular spectroscopy.

(i) Bohr condition

(ii) Vibrational energy

(iii) Rotational energy

(b) Consider the transition from $E_0 \rightarrow E_m$ of a molecule (M) between two energy levels, E_0 and E_m as depicted in the diagram below. Consider that the molecule (M) has components of nuclear (N), electronic (e), vibrational (V) and rotational (R) energy levels.



(i) State all the component transitions involved in the transition $E_0 \rightarrow E_m$.

(ii) What is the change in total energy (ΔE) of the molecule in the transition $E_0 \rightarrow E_m$?

(iii) Express the total energy change in terms of nuclear, electronic, vibrational and rotational energy changes?

(30 Marks)

Answer either **Part (C)** <u>or</u> **Part (D)** (but **NOT** both)

Part C

(a) What is the gross selection rule and the specific selection rule for pure rotational spectroscopy of a rigid diatomic molecule?

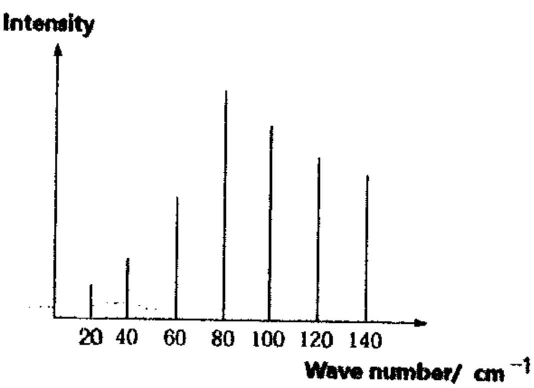
(b) Part of the microwave spectrum of the above diatomic molecule, XY, recorded by a student, is shown in the figure below. The relative atomic masses of X and Y are 1.0 and 35.0, respectively.

(i) Deduce whether XY behaves as a rigid rotor or a non-rigid rotor.

(ii) Assign each of the above absorption lines to a particular transition.

(iii) Calculate the moment of inertia, I, of the molecule XY.

Given that: $\bar{\nu}_J = 2\bar{B}\,(J+1)$



(40 Marks)

Part D

(a) (i) Name two (02) factors that determine the width of a peak.

(ii) Consider a gaseous sample of molecules which gives a peak (centred) at the frequency (ν) in its absorption spectrum.
With the aid of an absorption spectrum explain what will happen to the width of the peak when the temperature of the sample increases from $T_1 < T_2 < T_3$.

(b) A sample Z has only two energy levels. The energy difference between the two levels is 6.63×10^{-28} J. A gaseous sample of three different molecules, P, Q and R is placed in a spectrometer. In this sample, P moves towards, and R moves away from the radiation source of the spectrometer with the same speed of 6×10^{7} ms^{-1}. Q is stationary with respect to the source.
Calculate the frequencies of the radiation in the beam of the spectrometer at which P, Q and R may absorb radiation.

(40 Marks)

2. Answer **all parts A and B**

Part A

The experimetal set up used in the Hittorf method to find out the transport number of Zn^{2+} is shown in figure 1.
In this method, each compartments was filled with 400 cm^3 of 0.020 mol dm^{-3} $ZnCl_2$ solution and a current of 1.0 A was supplied for10 minutes using a battery. After completing this experiment, the student **confirmed he had done this experiment correctly** by measuring the Zn^{2+} concentration in the middle compartment.
The concentration of Zn^{2+} and the volume of solution in the left compartment are 0.015 mol dm^{-3} and 400 cm^3 respectively.
(The molar mass of Zn is 65 g mol^{-1})

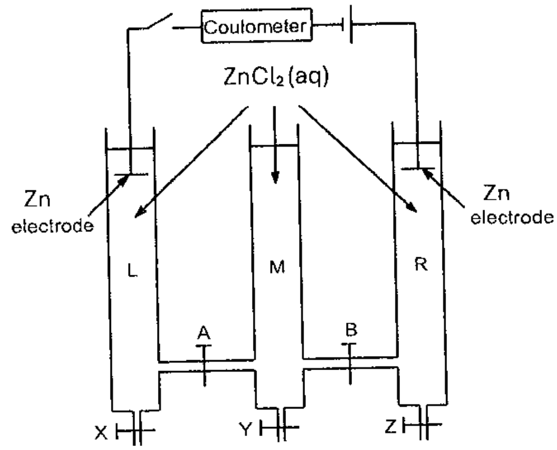


Figure 1

(i) What is the expected concertation of Zn^{2+} in the middle compartment if he had done this experiment correctly?
(ii) What is the charge generated by the battery?
(iii) Write down the reactions at the left and right compartment separately.
(iv) Derive the relationship between the change of Zn^{2+} moles (ΔN_L)in the left compartment and the transport number of Zn^{2+} ($t_{Zn^{2+}}$).
(v) Determine the transport number of Zn^{2+} and Cl^-.

(60 marks)

Part B

A student performed conductimetric titration to plot a titration curve for the titration between a strong acid and a strong base. In this titration, 10.0 cm^3 of 0.010 mol dm^{-3} H_2SO_4 was titrated with 0.010 mol dm^{-3} NaOH. The molar conductivities of H^+ and SO_4^{2-} are 2.5 x10^{-2} S m^2 mol^{-1} and 8.0 x10^{-3} S m^2 mol^{-1} respectively.

(i) Determine the ionic mobility of H^+ in $cm^2\ V^{-1}s^{-1}$.

(ii) Write down the relationship between the molar conductivity of H_2SO_4 solution with the molar conductivity of ionic species using the standard symbols.

(iii) Calculate the conductivity of the H_2SO_4 solution (in **mS cm⁻¹**) before starting the titration with NaOH.

(iv) Briefly explain the expected titration curve for the above titration.

(40 marks)

3.

(a) (i) Write down the **logarithmic form** of the **Arrhenius equation**. Identify the independent and dependent variables that produce a linear relationship.

(ii) The following results were reported from a kinetics experiment to test the relationship between temperature and rate constant. Carry out an **appropriate tabulation** of data required to plot a suitable graph in accordance with the logarithmic form of the Arrhenius equation you wrote in (i) above. (You **do not** need to plot a graph)

Temperature/°C	27	37	47	57	67
$k \times 10^4/\text{min}^{-1}$	7.5	15.0	20.5	35.0	50.0

(25 marks)

(b) (i) Define the terms "**Rate Determining Step (RDS)** and "**Steady State Approximation (SSA)** as applied in multi–step reaction mechanisms in chemical kinetics.

(ii) When CH_3CHO molecules are subjected to thermal decomposition, several reactive intermediates are formed as shown in the following multi–step reaction mechanism. Note that each of these steps is an elementary reaction with specific rate constants as shown.

$CH_3CHO \xrightarrow{k_1} CH_3^{\bullet} + CHO^{\bullet}$ (fast)

$CH_3^{\bullet} + CH_3CHO \xrightarrow{k_2} CH_4 + CH_3CO^{\bullet}$ (slow)

$CHO^{\bullet} \xrightarrow{k_3} H^{\bullet} + CO$ (fast)

$CH_3CO^{\bullet} \xrightarrow{k_4} CH_3^{\bullet} + CO$ (fast)

$H^{\bullet} + CH_3^{\bullet} \xrightarrow{k_5} CH_4$ (fast)

(a) Giving reasons, identify the rate determining step and write the differential form of the rate law for this reaction mechanism.
(b) What is the overall order of the thermal decomposition reaction of CH_3CHO?
(c) Identify all the intermediates involved in this reaction mechanism.
(d) Write down the overall reaction for the thermal decomposition of CH_3CHO.
(e) Applying the steady state approximation for the intermediates, $CHO^{\bullet}$ and $H^{\bullet}$, show that

$$[H^{\bullet}] = \frac{k_1[CH_3CHO]}{k_5[CH_3^{\bullet}]}$$

(45 marks)

(c) A drug is known to be ineffective when it has undergone 30% decomposition. The original concentration of this drug is 500 units/mL at 298 K. A sample of this drug was analyzed after 20 months, and it was found to have a concentration of 420 units/mL at 298 K.

Assuming that this decomposition follows first order kinetics, calculate the following at 298 K.

i) The rate constant of the decomposition reaction.
ii) Expiration time of the drug.
iii) The half–life.

($ln\frac{[A_o]}{[A]} = kt$ is the integrated form of the rate equation for 1st order kinetics and the symbols used have their usual meanings)

(30 marks)

4. (a) Define the following terms.

(i) Components (C)
(ii) Degrees of Freedom (F)
(iii) Triple point (T)

(15 Marks)

(b) The triple point of water occurs at 273.16 K and 0.006 atm.
Sketch a fully labelled phase diagram for one component (water) system and indicate the normal melting point and boiling point on it.

(20 Marks)

(c) Two liquids 46.0 g of A (C_7H_8) and 80.0 g of compound B were mixed at room temperature. The vapour pressures of pure A and pure B at this temperature are 50 torr and 30 torr respectively. If the total vapour pressure of the mixture is 42 torr, calculate

(i) The molar mass of B (in g mol^{-1}) and

(ii) The vapour composition corresponding to the above mixture at room temperature.
(assume ideal behavior and total miscibility for all compositions)

(iii) Sketch a fully labelled boiling point vs composition phase diagram to represent the above system indicating all the relevant regions, curves and points.

(35 Marks)

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

<u>Part A</u>

(a) The normal boiling points of pure liquids, A and B, respectively, are 160°C and 200°C. An equimolar mixture of A and B forms an azeotrope whose normal boiling point is 150°C.

With the aid of the sketch of the Temperature *vs* Composition phase diagram for the above system, briefly outline the result of carrying out fractional distillation corresponding to a mixture whose composition is

(i) the azeotrope (ii) given as mole fraction of A = 0.4

(30 Marks)

<u>Part B</u>

(a) Two metals M and N (melting point of M = 1100°C; melting point of N = 800°C) are said to form a simple eutectic system. The eutectic composition corresponds to a melt containing 6 moles of M and 3 moles of N. The cooling curve corresponding to the eutectic composition shows a 'halt" at 550°C.

(i) Sketch a fully labelled phase diagram for the above system.

(ii) Sketch a cooling curve corresponding to 70 mol % of M..

(30 Marks)