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	**: 2021/2022**
Date	**: 23.10.2022**
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)	=	$8.314\ J K^{-1}\ mol^{-1}$
Avogadro constant (N_A)	=	$6.023\times10^{23}\ mol^{-1}$
Faraday constant (F)	=	$96,500\ C\ mol^{-1}$
Planck constant (h)	=	$6.63\times10^{-34}\ J\ s$
Velocity of light (c)	=	$3.0\times10^{8}\ m\ s^{-1}$
Standard pressure	=	$10^5\ Pa(N\ m^{-2})$ = 1 bar
Protonic charge (e)	=	$1.602177\times10^{-19}\ C$
π	=	3.14159
$Log_e(X)$	=	$2.303\ Log_{10}(X)$

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

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

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

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

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

Part A

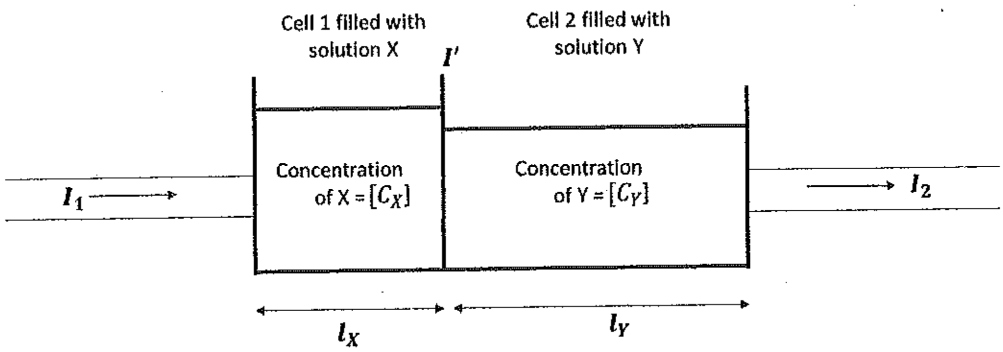
(a) Given that the intensities of incident and outgoing beams of monochromatic radiation from an absorbing sample as **I** and **I′**, respectively. The absorbance of the sample (**A**), Concentration of the sample (**C**) and the path length of the cell is (***l***).
Define the following terms using the above information provided.

(i) Transmittance of the sample
(ii) Absorbance of the sample
(iii) Molar extinction coefficient

(18 Marks)

(b) A student performed an experiment with two adjacent cells (cell 1 and cell 2) partially filled with two dilute aqueous solutions from two different colored solutions X and Y as indicated in the following diagram. The concentrations of two solutions $[C_X]$ and $[C_Y]$ are, 0.12 $moldm^{-3}$ and 0.18 $moldm^{-3}$ respectively. And the width of two cells, are $l_X = 0.2$ m and $l_Y = 0.3$ m respectively.

This student passed a narrow parallel beam of visible radiation through the two cells as indicated in the figure below.



The intensity, of the incident beam I_1 is 7.5×10^{-5} $\text{Js}^{-1}\text{m}^{-2}$. The molar extinction coefficients ε_X and ε_Y in units $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ are 0.18 and 0.09 respectively. Assume that the intensity of the outgoing radiation from the cell 1 and the incoming radiation to the cell 2 is I' and there is no any loss due to scattering and reflection at the border and the walls of the cells and the solvent do not absorb any visible radiation.

(i) Based on the information provided, calculate the absorbance of the samples in the cell 1 and cell 2. Write down all the equations that you used for the calculation.

(ii) Derive a relationship between the intensity of incoming beam I_1 and intensity of the outgoing beam I_2 using the symbols $[C_X]$, $[C_Y]$, ε_X, ε_Y and l_X, l_Y.

(iii) Calculate the intensity of the outgoing beam, I_2.

(32 Marks)

Part B

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

(i) Gross selection rule

(ii) Specific selection rule

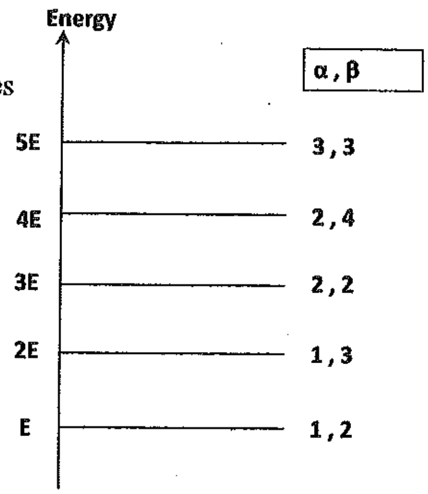
(iii) Allowed transition

(12 Marks)

(b) Consider a (hypothetical) gaseous molecule which has only five (05) energy levels. It is known that the population of the two upper most levels are zero at 30 °C. What is the maximum number of peaks observable in the absorption spectrum of this molecule at 30 °C.

(08 Marks)

(c) If these five energy levels of the above molecule are at energies E, 2E, 3E, 4E and 5E and they are labelled by two quantum numbers (**α, β**). The energies and the values of quantum numbers are shown in figure to the right. The specific selection rules in absorption spectroscopy of the molecule are **$\Delta\alpha = \pm1$ and $\Delta\beta = 0, \pm1$.**



(i) Giving reasons deduce the maximum number of lines that can be observed in the absorption spectrum of the molecule, taken at 30°C.
Indicate the corresponding energy level transition/s in standard form as **$(\alpha_1, \beta_1) \rightarrow (\alpha_2, \beta_2)$**.

(ii) Calculate the frequency of the line with the lowest frequency in the absorption spectrum, if $E = 8.25\times10^{-22}$ J.

(30 Marks)

Part C

(a) Name two (02) effects that determines the width of a peak. **(10 Marks)**

(b) (i) Consider a gaseous sample of molecules which gives a peak (centered) at frequency **v** in its absorption spectrum. With the aid of the absorption spectra explain what will happen to the width of the peak when the temperature of the sample increases from $T_1 < T_2 < T_3$.

(15 Marks)

(ii) A molecule has only two (02) energy levels. The energy difference between the two energy levels is 6.63×10^{-28} J. A gaseous sample of it placed in a spectrometer. Consider three (03) gas molecules in this sample named as P, Q and R.
The molecule, 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 in the spectrometer at which P, Q and R may absorb radiation.

(25 Marks)

2. Answer **any two parts out of A, B and C**

Part A

(i) Define the following

- Charge number of an ion
- Transport number of an ionic species in a solution
- Molar conductivity of an electrolyte or an ionic species in a solution

(ii) Calculate the charge (in Coulombs) of 3.0 mol of Hg_2^{2+} ions.

(iii) At 25^0C and 1 atm the conductivity of a saturated solution of AgCl is 25 x 10^{-4} Sm^{-1}. Calculate the solubility product of AgCl at 25^0C and 1 atm. (Limiting molar conductivities in units of S m^2mol^{-1} at 25^0C and 1 atm; Ag^+ = 0.0062, Cl^- = 0.0076).

(iv) In the moving boundary method, the apparatus consists of two chambers named A and B. Consider that the chamber B (upper) is filled with KCl solution and chamber A (lower) is filled with the following solution $CdCl_2$.

- Why $CdCl_2$ solution is kept in the lower chamber?
- Give reasons why it is not possible to use $Cd(NO_3)_2$ as the following solution in this experiment.
- Why is it necessary to maintain the boundary between the two solutions inside the tube with a small cross-sectional area?
- The cation in the following solution should have a smaller ionic mobility than the cation whose ionic mobility is measured. Explain why?

(50 Marks)

Part B

(i) Write down the equation relating the transport number, t_B, ionic mobility, u_B, and identify all the parameters in it.

(ii) Calculate the transport number of Cl^-(aq) in an aqueous solution which is 0.001 $moldm^{-3}$ in $MgCl_2$ and 0.002 mol dm^{-3} in NaCl at 25^0C and 1 atm. State assumptions you make in the above calculation.
Ionic mobilities at infinite dilution of (at 25^0C and 1 atm) Mg^{2+} = 55.0 x 10^{-9} $m^2V^{-1}s^{-1}$, Na^+= 52.0 x10^{-9} $m^2V^{-1}s^{-1}$ and Cl^- = 79.0 x 10^{-9} $m^2V^{-1}s^{-1}$.

(iii) Explain how the charge asymmetry and electrophoretic effect reduce the ionic mobility with increasing electrolyte concentration in a solution?

(50 Marks)

Part C

(i) Describe the limiting molar conductivity of an ionic species and an electrolyte.

(ii) Limiting molar conductivities of NaCNS, $Ca(NO_3)_2$ and $NaNO_3$, in units of Sm^2mol^{-1} at 25^0C and 1 atm are 0.112, 0.0260 and 0.0121 respectively. Calculate the limiting molar conductivity of $Ca(CNS)_2$ at 25^0C and 1 atm.

(iii) The conductivity of a saturated solution of barium sulphate at 298K is found to be 4.20 x 10^{-4} S m^{-1}. Limiting molar conductivity of $BaSO_4$ is 2.865 x 10^{-2} S m^2 mol^{-1}. Calculate the solubility of $BaSO_4$. Conductivity of water is 1.05 x 10^{-4} S m^{-1}.
(RAM of Ba = 137, S = 32, O=16)

(iv) Sketch the graphs for the following conductometric titrations, when the base is the titrant.

- strong acid - strong base and
- strong acid - weak base

(50 Marks)

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

(ii) A student tries to obtain a part of the microwave spectrum of a rigid diatomic molecule, $H^{35}Cl$.

(A) Determine the positions (wavenumbers) of the first four transitions, which involved the lowest frequency radiation, in the microwave absorption spectrum of $H^{35}Cl$.

(B) Draw the possible absorbance *vs* wavenumber microwave spectrum of $H^{35}Cl$ molecule by assigning the positions in the spectrum you obtained in (ii) (A) above.

(C) If the rotational constant of the molecule, $H^{35}Cl$ is 25.20 cm^{-1}, indicate the corresponding transitions that this student can observe.

[Hint: $\bar{\nu}_J = 2\bar{B}(J + 1)$]

(30 Marks)

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

(ii) Derive or write down the **logarithmic form of the Arrhenius equation** and identify the gradient, independent and dependent variables that produce a liner relationship.

(iii) The following results were reported from a kinetic 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 obtained in (ii) above. (You **do not** need to plot a graph)

Temperature/°C	27	37	47	57	67
$k \times 10^3/min^{-1}$	7.5	15.0	20.5	35.0	50.0

(30 Marks)

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

(ii) Consider the following multi–step reaction mechanism.

$$RCHO \overset{k_1}{\rightarrow} R^* + CHO^* \text{ (fast)}$$

$$R^* + RCHO \overset{k_2}{\rightarrow} RH + RCO^* \text{ (slow)}$$

$$RCO^* \overset{k_3}{\rightarrow} R^* + CO \text{ (fast)}$$

$$2RCO^* \overset{k_4}{\rightarrow} RCOCOR \text{ (fast)}$$

(A) Giving reasons, identify the rate determining step and write the rate law for this reaction mechanism.

(B) Identify all the intermediates of this reaction mechanism.

(C) Applying the steady state approximation for R^*, show that $[R^*] = \frac{k_1}{k_2} + \frac{k_3[RCO^*]}{k_2[RCHO]}$

(32 Marks)

(d) Consider the following elementary reversible reaction.

$$2\,X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 3\,Y$$

Write down the rate equation for this elementary reversible reaction in terms of $\frac{d[X]}{dt}$

(08 Marks)

4. (a) (i) Write down the expression for the Gibb's phase rule and define all the terms in it.

(ii) Sketch a clearly labelled pressure vs Temperature phase diagram for a pure substance X (one component system). Label all the regions and the triple point in your diagram.

(iii) Apply Gibb's phase rule to all three (03) regions (label them as S, L, V) and the triple point separately and determine the number of degrees of freedom.

(30 Marks)

(b) Two liquids A and B are miscible each other for all compositions and form ideal binary solution. When the system is in equilibrium at room temperature, 46.0 g of liquid A and 80.0 g of liquid B, are present in the liquid phase. The vapor pressure of pure A and pure B are 50 torr and 30 torr respectively. If the total vapor pressure of the mixture is 42 torr. Given that molar mass of A is 92 $gmol^{-1}$.

(i) Calculate the molar mass of B (in $gmol^{-1}$).

(ii) Calculate the vapor composition of B corresponding to the above mixture at room temperature.

(iii) Draw a fully label pressure *vs* composition (X_A) phase diagram to represent the above mixture at room temperature.

(40 Marks)

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

Part A

(a) The normal boiling points of pure liquids, P and Q, respectively, are 260 °C and 300 °C. An equimolar mixture of P and Q forms an azeotrope whose normal boiling point is 250 °C.

(i) Sketch a fully labelled Temperature vs Composition (X_P) phase diagram for the above system.

(ii) What type of deviation from Raoult's law occurred in the above azeotropic mixture?

(iii) With the aid of the above sketch briefly outline the result of carrying out fractional distillation corresponding to a mixture whose composition is

(A) The azeotrope

(B) Given as mole fraction of P is 0.4.

(30 Marks)

Part B

(a) The phase diagram for A-B at constant pressure shows that a compound, A_3B_2 is formed with congruent melting point of 600 °C. The melting points of pure A is 500 °C and that of B is 800 °C. The two eutectic compositions and their temperatures are given below. The eutectic composition (X) formed at 300 °C at the mole fraction of B 20%. And the eutectic composition (Y) formed at 400 °C at the mole fraction of B 60%.

(i) Sketch a fully labelled Temperature vs Composition (X_B) phase diagram for the above system.

(ii) Sketch the cooling curves corresponding to following mixtures and indicate "break" and "halt" points clearly in the cooling curves you have drawn.

(I) A melt corresponding to the mole fraction of B at 30%.

(II) A melt corresponding to the mole fraction of B at 60%.

(30 Marks)