00692

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

Course Code	**: CYU4301**
Title	: Concepts in Chemistry
Department	: Chemistry
Level	: 04
Name of the Examination	: Final Examination
Academic Year	: 2020 /2021
Date	: 30th December 2021
Time	: 9.30 am to 11.30 am
Duration	: 2 hours

General Instructions

1 This question paper consists of 04 **(Four)** questions in 08 pages
2. Read all instructions carefully before answering the questions
3. Answer all **04 (Four)** questions.
4. Having any unauthorized documents/ mobile phones/any other electronic equipment in your possession is a punishable offence.
5. Use blue or black ink to answer the questions.
6. Clearly write your index number in all pages of your answer script.
7. The use of a non-programmable electronic calculator is permitted

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

Part A

1. You are provided with two (02) solutions X and Y containing two (02) non-interacting chemical species A and B in each solution. The ratio of concentrations of A and B (C_A:C_B) in solution X is 1:1 while that in solution Y is 1:2. In an experiment, it is observed that when a portion of solution X is held in a cell of pathlength 1.0 cm and at 25 °C, the incident intensity of radiation at wavelength λ goes down by 40% when a beam of radiation travels through the sample. When the measurement is repeated with solution Y under identical experimental conditions, the incident intensity of radiation at wavelength λ goes down by 50% when a beam of radiation travels through the sample. It is given that the concentration of A in both solutions X and Y is 1.00 mol dm^{-3}.

(a) Based on the information provided, calculate the molar absorption coefficients of species A and B at wavelength λ.

(30 marks)

(b) Predict the absorbance (A) of a third solution Z containing A and B in a concentration ratio 1:3 while the concentration of A is 2.00 mol dm^{-3} if the same experiment above is repeated at 25 °C and at wavelength λ with solution Z.

(15 marks)

(c) Briefly explain how your calculations in parts (a) and (b) should change if species A and B were NOT said to be non-interacting.

(05 marks)

Part B

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

(i) Dipole moment

(ii) Permanent dipole moment

(iii) Induced dipole moment

(15 marks)

(b) Estimate the dipole moments of o-chlorotoluene and m-chlorotoluene if the dipole moments of toluene and chlorobenzene are 0.40 D and 1.57 D, respectively.

(Hint: $\mu^2 = \mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 cos\theta$)

$[cos(60°) = \frac{1}{2}\ ,\ sin(60°) = \frac{\sqrt{3}}{2}\ ,\ cos(120°) = -\frac{1}{2}\ ,\ sin(120°) = \frac{\sqrt{3}}{2}\ ]$

(20 marks)

(c) Draw a structure of o-chlorotoluene and m-chlorotoluene and indicate the direction of the dipole moment you calculated above. **(15 marks)**

Part C

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

i) Bohr condition
ii) Vibrational energy
iii) Mixed transition **(15 marks)**

(b) Two energy levels, E_x and E_y, of a molecule A has the following components of nuclear (N), electronic (e), vibrational (V), and rotational (R) energy levels.

$$E_x = N_1 + e_5 + V_3 + R_{10}$$
$$E_y = N_3 + e_3 + V_5 + R_5$$

i) State all the component transitions involved in the transition $E_x \rightarrow E_y$.
ii) Predict the number of lines that could be observed in the absorption spectrum of molecule A produced by the transition $E_x \rightarrow E_y$. Briefly explain how you arrived at the answer.
iii) In what region of the electromagnetic spectrum does the spectral feature/s produced by the transition $E_x \rightarrow E_y$ **most likely** to appear? Briefly explain.

(20 marks)

(c) Show that all the molecules in a sample must be in the ground energy level at absolute zero temperature. **(15 marks)**

Hint: $N_i = \frac{g_i}{g_0} N_0 \times \exp\left(-\frac{(E_i - E_j)}{kT}\right)$

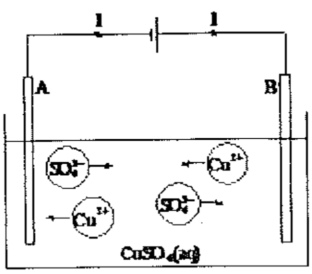
2. Answer any **TWO (2) parts** out of (a),(b) and (c)

(a) (i) Define the following terms;

(A) Drift speed of an ion
(B) Electric field strength
(C) Molar conductivity of an electrolyte

(ii) Deduce the SI units of resistivity and conductivity

(iii) A student electrolysed a copper sulphate solution using two Pt electrodes, A and B (See figure below)



The directions of movement of the copper and sulphate ions are shown in this figure. The student noted that 1.5×10^{-5} mole and 3.0×10^{-5} mole of sulphate and copper ions, respectively, passed through a cross section of the solution in between electrodes A and B in one second.

(A) Giving reasons state the magnitude of the current through the solution.

(B) Calculate the total charge delivered by the battery.

(C) Giving reasons, identify the anode and cathode.

(D) Which direction does the electric current flow through the solution, A to B or B to A? Explain.

(iv) The conductivity of a 0.02 mol dm^{-3} solution of KCl was found to be 0.00277 S cm^{-1} with a resistance of 83 Ω. When the KCl solution was substituted with a 0.005 mol dm^{-3} K_2SO_4 solution, the resistance was 326 Ω. Calculate the cell constant and the molar conductivity of K_2SO_4 solution.

(50 marks)

(b) (i) Define the following terms;

(A) Ionic mobility of an ionic species
(B) Transport number of an ionic species in a solution

(ii) Moving boundary experiment was applied to a 0.1mol dm^{-3} aqueous KCl solution at 25 ^{0}C and 1 atm, using aqueous $CdCl_2$ as the following solution. The boundary moved 4.64 cm in 67 minutes when the current is at a constant value of 5.21×10^{-3} A. The cross-sectional area of the tube is 0.23 cm^2 and the conductivity of the electrolyte is 1.29 S m^{-1} at 298 K.

(A) Calculate the electric field strength,
(B) the ionic mobility and
(C) the transport number of K^+ in the solution.

(iii) At 298 K, the conductivity of a saturated solution of AgCl was found to be 2.28×10^{-4} S m^{-1}. At this temperature, the molar conductivities of aqueous Ag^+ and Cl^- ions are 0.00619 S m^2 mol^{-1} and 0.00752 S m^2 mol^{-1} respectively. Calculate the solubility product of AgCl at 298K.

(50 marks)

(c) (i) Consider a solution of weak monobasic acid, HA, where the degree of dissociation of HA is α. Starting with the definitions of molar conductivity of an electrolyte and an ionic species, show that in this solution, $\Lambda_{HA} = \alpha(\lambda_{H^+} + \lambda_{A^-})$

where $\Lambda_{HA} = molar\ conductivity\ of\ HA;\ \lambda_{H^+} = molar\ conductivity\ of\ H^+$
$\lambda_{A^-} = molar\ conductivity\ of A^-$

(ii) Molar conductivity of a 0.01mol dm^{-3} solution of a weak acid, HA, at 298 K is 5.17×10^{-4} S m^2 mol^{-1}. At this temperature, the limiting molar conductivities of H^+ and A^- are 3.50×10^{-2} S m^2 mol^{-1} and 0.40×10^{-2} S m^2 mol^{-1}, respectively.

Calculate (A) the degree of dissociation
(B) dissociation constant for HA

(iii) (A) The relationship between limiting molar conductivity of an ionic species and its limiting ionic mobility is given below. Identify all the parameters in it.

$$\Lambda_Y^0 = \sum \left(\frac{C_B}{C_Y}\right) u_B^0 |Z_B| F$$

(B) Why is the limiting molar conductivity of SO_4^{2-} ion nearly double that of Br^- ion?

(50 marks)

3. (a) Four consecutive absorption lines appear in the microwave spectrum of gaseous AB molecules at 75.624 cm^{-1}, 100.832 cm^{-1}, 126.04 cm^{-1}, and 151.248 cm^{-1}. Relative atomic masses of A and B are given to be 26.980 and 1.00 respectively.

(i) Show that AB behaves as a rigid rotor.
(ii) Determine the rotational quantum numbers associated with the highest energy absorption line in the microwave spectrum of AB.
(iii) Calculate the equilibrium bond length of AB.
[Hint: $\bar{\nu_J} = 2\bar{B}(J+1)$, $I = \mu R^2$, $\bar{B} = \frac{h}{8\pi^2 Ic}$] **(30 marks)**

(b) The rate constant (k) for a hypothetical elementary reaction of the form 2A-----> P is reported to be 1.0×10^{-4} mol^{-1} m^3 min^{-1} at 300 K

(i) Determine the value of the rate constant in terms of **mol^{-1} dm^3 s^{-1}**

(ii) Given that $kt = \frac{x}{a(a-x)}$ is the integrated form of the rate equation [where a = initial concentration and x = concentration change in time t], calculate the time taken in seconds at 300 K for the reduction of the concentration from 0.75 mol dm^{-3} to 0.25 mol dm^{-3}. **(30 marks)**

(c) A drug is known to be ineffective when it has undergone 30% decomposition. A sample of this drug whose original concentration is given as 500 units/ml was analysed after 20 months; it was found to have a concentration of 420 units/ml. Assuming that this decomposition follows **first order kinetics,** calculate the expiration time of this drug and its half-life.

[$t = \frac{1}{k} ln \frac{A_o}{A}$ *is the integrated form of the rate equation for first order kinetics; the symbols used have their usual meanings*] **(24 marks)**

(d) (i) Consider the following reversible reaction

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

It is said to be second order in the forward direction and first order in the reverse direction. Write down the rate equation in terms of $-\frac{d[A]}{dt}$

(ii) Consider two consecutive irreversible **first order** reactions given by a general equation of the form $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ (k_1 and k_2 are the respective rate constants; $k_1 \neq k_2 \neq 0$).

Write down the equation for the rate of formation of B

(16 marks)

4. (a) (i) Write down the symbolical expression for Raoults Law with respect to a component forming an ideal binary solution. Identify all the symbols in it.

(ii) Derive the following expression for total pressure (P_T) with respect to an ideal mixture formed by two liquids, A and B (All standard symbols have been used)

$$P_T = x_B (P^o_B - P^o_A) + P^o_A$$

(16 mark)

(b) An ideal solution is prepared by dissolving 7.8 g of benzene in 92.0 g of toluene at 25 °C. The vapour pressures of pure benzene and pure toluene are 12.7 kPa and 3.8 kPa respectively at this temperature. [H = 1, C = 12, O = 16]

(i) Determine the partial vapour pressure of each of the two components for the mixture

(ii) Calculate the vapour composition corresponding to the above mixture in terms of mole fraction of Benzene

(24 marks)

(b) (i) Sketch a clearly labelled temperature vs composition (at 1.0 atm pressure) phase diagram corresponding to the Nitric acid and water system that shows negative deviation from ideal behaviour. The composition of the corresponding azeotrope is given as 68% Nitric Acid by mass [H = 1, N = 14, O = 16; boiling point of Nitric acid is 86 ^{0}C]

(ii) Determine the mole fraction of Nitric acid in the above azeotropic mixture.

(iii) Fractional distillation of an Azeotropic mixture does not allow separation of the two components in the mixture. Why? (Experimental details NOT necessary)

(30 marks)

Answer either part (A) or (B) (but NOT both).

(A) (a) 20.00 cm^3 of a liquid A [relative molar mass 96 and density 1.2×10^3 kg m^{-3}] is mixed with 40.00 g of a liquid B. If the mole fraction of A in this fully miscible system is $\frac{1}{3}$, determine the relative molar mass of B.

(18 marks)

(b) What do you understand by the following terms?

(i) An ideal binary solution

(ii) An Azeotrope

(12 marks)

(B) Two metals A and B (melting point of A > melting point of B] are said to form a simple eutectic system at elevated temperatures. Mole fraction of A is 1/3 at the eutectic point. The cooling curve corresponding to an equimolar mixture of A and B shows a **"break"** at 700 °C and a **"halt"** at 550 °C

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

(ii) Identify the **break, halt** and **eutectic point**; mark these points on the above phase diagram

(iii) What is meant by a "break" and a "halt"? Use the phase rule to explain.

(30 marks)