UNIVERSITY OF RUHUNA

BACHELOR OF SCIENCE GENERAL DEGREE (LEVEL II) SEMESTER I

EXAMINATIONS – JULY/AUGUST 2023

SUBJECT: Chemistry

COURSE UNIT: CHE 2122 (Physical Chemistry II) **TIME: Two (02) hours**

Answer **four (4)** questions only by selecting **two (2)** from each of the sections A and B.

Avogadro's constant (N_A)	$= 6.022 \times 10^{23}$ mol^{-1}
Atomic mass unit (amu)	$= 1.6606 \times 10^{-27}$ kg
Boltzmann constant (k_B)	$= 1.3806 \times 10^{-23}$ J K^{-1}
Electron charge (e)	$= -1.602 \times 10^{-19}$ C
Electron mass (m_e)	$= 9.109 \times 10^{-31}$ kg
Faraday constant (F)	$= 9.6485 \times 10^{4}$ 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)	$= 6.626 \times 10^{-34}$ J s
Proton mass (m_p)	$= 1.673 \times 10^{-27}$ kg
Speed of light (c)	$= 2.998 \times 10^{8}$ m s^{-1}
Vacuum permittivity (ε_0)	$= 8.854 \times 10^{-12}$ J^{-1} C^2 m^{-1}

Important conversion factors

1 atm = 760 mmHg = 1.01325 bar = 101325 Pa

2.303 (RT/F) = 59.15 mV at 298.15 K

Section A

1. Answer all parts.

a) Light possesses both wave-like and particle-like properties. The latter is illustrated by the photoelectric effect.

(i) Write down two experimental observations on the photoelectric effect that could not be explained by classical physics.

(08 marks)

(ii) Express the kinetic energy of the ejected electron (KE) in terms of the frequency of the incident light (ν) and the threshold frequency of the electron (ν_0).

(04 marks)

(iii) The threshold frequency for ejecting an electron from a metal surface is 5.84×10^{14} Hz. Will red light with a wavelength of 650 nm eject electrons from the metal surface? (Show necessary calculations to justify your answer) (08 marks)

(b) The state of a quantum mechanical system is completely described by a wavefunction $\psi(r, t)$.

(i) Write down four characteristics of a well-behaved wavefunction.

(04 marks)

(ii) Decide whether the function $\psi(x) = e^{-x}$ is well behaved over $0 \leq x \leq \infty$. If it is well-behaved, find the normalization constant to normalize it.

(16 marks)

(c) In quantum chemistry, the observables in classical mechanics are represented by mathematical operators. Consider a particle of mass m travelling along the x-axis.

(i) Write the quantum mechanical operator ($\hat{p}_x$) for the linear momentum of the particle.

(04 marks)

(ii) Construct the Hamiltonian operator using $\hat{p}_x$ and express the time-independent Schrödinger equation for the particle if the potential energy of the particle is zero.

(16 marks)

(iii) If the wavefunction $\psi(x) = Ae^{ikx}$ (where k is any constant) is a solution to the Schrödinger equation, calculate the total energy (E) of the particle. Is it quantized? Justify your answer.

(15 marks)

(iv) Calculate the momentum and direction of the particle using the relevant operator.

(10 marks)

(v) If the particle is also allowed to move in the opposite direction with the same momentum, construct a general wavefunction that describes the particle's motion in $\pm x$ directions.

(15 marks)

02. Answer all parts.

The experimental absorption spectra of trans-polyene can be used to determine the box length in the one-dimensional particle-in-a-box (PIB) model.

(a) The one-dimensional PIB model consists of a particle moving parallel to the x-axis between two impenetrable walls. The potential energy of the particle is zero along the box and rises straight up at the walls to infinity to keep the particle in the box.

(i) Write down the time-independent Schrödinger equation for the particle in the box. The mass of the particle is m.

(05 marks)

(ii) The Schrödinger equation for the particle can be solved exactly to find the solution $\psi(x)$. It has the following form.

$$\psi(x) = N \sin\left(\frac{n\pi x}{L}\right) \qquad (0 \leq x \leq L) \text{ and } (n = 1, 2, 3, \dots)$$

where L is the length of the box.

I. Calculate the normalization constant N.

II. Obtain the following expression for the total energy of the particle by solving the Schrödinger equation as an eigenvalue problem.

$$E_n = \frac{n^2 h^2}{8mL^2}$$

Useful relation:

$$\int \sin^2(ax)dx = \frac{x}{2} - \frac{\sin(2ax)}{4a}$$

(30 marks)

(iii) Plot the first four solutions (wavefunctions) of the model as a function of x $(0 \leq x \leq L)$.

(08 marks)

(iv) These wavefunctions represent de Broglie waves. Using your plot, find a relationship between the de Broglie wavelength λ and the length of the box L.

(05 marks)

) The lowest energy band in the absorption spectrum of 1,3-butadiene was observed at 217 nm.

(i) For 1,3-butadiene, derive an expression for the energy difference between the highest occupied energy level and the lowest unoccupied energy level in the PIB model. Neglect the interaction between the electrons.

(14 marks)

(ii) Using the given wavelength, estimate the experimental box length for butadiene.

(14 marks)

(iii) Assuming that the average bond length of a carbon-carbon bond in the conjugated backbone is 1.40 Å, calculate the theoretical box length for 1,3-butadiene. If the calculated bond length differs from the experimental length, give a possible reason for the mismatch.

(10 marks)

(iv) Using the experimental box length you obtained for butadiene in the PIB model, answer the following questions.

I. Plot the π electron probability density for the highest occupied energy level. Hence, determine the most probable locations (x coordinates) of the electron in the same energy level.

II. Calculate the de Broglie wavelength for an electron in the highest occupied molecular orbital (HOMO).

(14 marks)

03. Answer all parts.

(a) (i) Name two (**02**) examples found in nature that serve as evidence for surface energy behavior. (10 marks)

(ii) Stating examples, give a short account on capillary action. (10 marks)

(b) "The formation of association colloids is spontaneous, provided the concentration of the amphiphile in solution exceed CMC"

(i) Give the reason for spontaneity of the above-mentioned process.

(ii) What is CMC? Write a short account on formation of micelles.

(20 marks)

(c)

(i) Sketch the following adsorption isotherms and give the main features of your sketch.

I the Langmuir adsorption isotherm

II the BET adsorption isotherm

(30 marks)

(ii) From the Langmuir adsorption isotherm equation, $\theta = \frac{Kp}{1+Kp}$, derive the linear form of the same.

(10 marks)

(iii) In an experiment carried out on investigation of adsorption of N_2 on Cu based catalyst, it was found that the adsorption process obeys the Langmuir isotherm behavior.

Using the experimental data, the linear form of Langmuir adsorption isotherm was plotted and the slope and the intercept were derived as 0.02 cm^{-3} and 2.05 Torr cm^{-3} g respectively.

Using the data of this experiment calculate the monolayer volume of N_2 gas and the adsorption equilibrium constant.

(20 marks)

Section B

04. Answer <u>all</u> parts

(a) Consider the molecules given below.

Cl_2, NO, N_2O, CH_4

(i) Find the number of vibrational and rotational modes in each of the above molecules.

(ii) Which of the above has/have infrared active vibrations? Give reasons.

(iii) Which of the above has/have Raman active vibrations? Give reasons.

(iv) Which of the above is/are microwave active? Give reasons.

(v) Which of the above is/are rotational Raman active? Give reasons.

(vi) Categorize the above molecules as linear, symmetric, and spherical rotors. Explain.

(40 marks)

(b) The vibrational frequency ν of a diatomic molecule is

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} - - - - - - -(1)$$

The vibrational energies of the molecule are given by

$$E = \left(n + \frac{1}{2}\right)h\nu - - - - - (2)$$

(i) Define all the terms in the two equations. (5 marks)

(ii) What is the model the above two equations are based on? (10 marks)

(iii) Calculate the reduced mass of C-H and C-D bonds in atomic mass unit. Assume that the mass of deuterium is twice that of hydrogen. (Relative atomic masses of H and C are 1.008 and 12.01, respectively) (10 marks)

(iv) If the C-H stretching frequency is 2900 cm^{-1}, find the corresponding C-D stretching frequency (in cm^{-1}) stating the assumptions you used. (15 marks)

(v) Calculate the zero-point vibrational energies (ZPE) of C-H and C-D stretching in kJ mol^{-1}. (10 marks)

(vi) Assume that the activation energy (E_a) for the C-H/C-D bond cleavage is approximately equal to the bond dissociation energy (BDE) and the Arrhenius factor is the same for both C-H and C-D bond cleavage.

I. Draw an appropriate diagram and show the BDE. Consider that the BDE is calculated with respect to the ZPE.

II. II. Find the relative rate constant for the C-H/C-D bond cleavage (kCH/kCD) at 25 °C.

(Hint: Arrhenius rate equation is given by $k = A\exp(-E_a/RT)$)

(10 marks)

05. Answer <u>all</u> parts.

(a) An electromagnetic wave has a wave number of 1800 cm^{-1}. Calculate the following for this radiation in the unit given within brackets.

(i) Wavelength (in nm)

(ii) Frequency (in THz)

(iii) Energy (kJ/mol)

(iv) Energy (eV)

(20 marks)

(b) The energy E_J of a rotational level J of a diatomic molecule is given by the following expression.

$$E_J = BhJ(J+1) \text{ where } B = \frac{h}{8\pi^2 I}$$

(i) Define all the terms in the above two equations and derive the unit of B.

(10 marks)

(ii) Calculate the frequency for the $J = 2 \rightarrow 3$ spectral transition of NO. The internuclear distance for NO is 200 nm. (N =14, O = 16)

(25 marks)

(iii) If the oxygen in NO is replaced by ^{18}O, predict the change in the value of the frequency for the same transition.

(15 marks)

(c) Certain diatomic molecules are both microwave and IR-active.

(i) Give an example of such a molecule. Explain the reason for your choice.

(ii) Assuming that each vibrational level has four rotational levels 0, 1, 2 and 3, sketch the rotation-vibration spectrum of this molecule for the transitions between the two vibrational levels $V = 0 \rightarrow 1$. Show P, Q, and R bands in the same diagram.

(30 marks)

06. Answer <u>all</u> parts

(a) The Grotthuss-Draper law is a fundamental principle in the field of photochemistry and it highlights the importance of light absorption in driving photochemical reactions. State the above law. (10 marks)

(b) Briefly explain why an excited triplet state always has a lower energy than that of the corresponding excited singlet state. (15 marks)

(c) Fluorescence and phosphorescence are both phenomena involving the emission of light from a substance after it has absorbed radiation. State two key distinctions between them. (10 marks)

(d) If 15% of the energy of a 100 W incandescent bulb generates visible light having average wavelength 600 nm, how many quanta of light are emitted in 10 minutes? (Incandescence is light emission due to intense heat). (20 marks)

(e) Oxalic acid is not decomposed directly by light of wavelength, 335 nm. However, irradiation in the presence of uranyl (UO_2^{+}) ion results in the decomposition of oxalic acid ($H_2C_2O_4$) to carbon monoxide , carbon dioxide and water.

(i) How do you explain this reaction? (05 marks)

(ii) Suggest a reaction sequence for the decomposition of the same. (10 marks)

(f) In photochemistry, quantum yield is used to quantify the efficiency of light absorption and subsequent photochemical reactions

(i) Define the term" Quantum yield". (10 marks)

(ii) The Stark-Einstein law sets the ideal condition where the maximum quantum yield would be 1. The actual value of quantum yield for a particular process is determined experimentally and can vary depending on the specific circumstances of that process. Using the photodissociation of HI as an example, explain the above statement.

(20 marks)

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