UNIVERSITY OF RUHUNA

BACHELOR OF SCIENCE GENERAL DEGREE (LEVEL II) SEMESTER I

EXAMINATIONS – FEBRUARY 2022

SUBJECT: Chemistry

COURSE UNIT: CHE 2122 **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

1 eV = 1.6022×10^{-19} J

Section A

01. Answer **all** parts.

(a) The failure of classical physics in explaining a set of experimental results collected towards the end of the 19th century motivated physicists to develop a new theory called quantum mechanics. Some of that evidence came from black-body radiation, photoelectric effect and spectroscopy

(i) Explain briefly the term "the ultraviolet catastrophe" and how it was resolved within Max Planck's quantum theory.

(20 marks)

(ii) (I) State the nature of light that Einstein used to explain the photoelectric effect.

(II) If electrons are ejected from a metal surface with kinetic energy of 4.3 eV when radiation of wavelength 195 nm shines on it, calculate the threshold frequency of the metal.

(20 marks)

(iii) Bohr model accounts for the hydrogen emission spectrum but fails to satisfy the Heisenberg Uncertainty Principle. Explain.

(10 marks)

(b) The Hamiltonian operator for a free particle of mass m confined in a two-dimensional rectangular box with dimensions a and b is

$$\hat{H} = -\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right]$$

where x $(0 \leq x \leq a)$ and y $(0 \leq y \leq b)$ coordinates are independent of each other.

(i) If the normalized wavefunction of the particle in the box is

$$\psi_{n,m} = \left(\frac{4}{ab}\right)^{1/2} \sin\frac{n\pi x}{a} \sin\frac{n\pi y}{b} \qquad \text{with } n, m = 1, 2, 3, \ldots$$

(I) Show that $\psi_{n,m}$ is an eigenfunction of the operator $\hat{H}$.

(II) Find the expected energy of the particle.

(20 marks)

(ii) Determine the most and least probable locations of the particle in the ground state.

(20 marks)

(iii) Using the part (b)-(i) above, show that for a particle in a *square* two-dimensional box, the second-lowest energy level is doubly degenerate.

(10 marks)

02. Answer **all** parts.

The wavefunction ψ contains all the information that can possibly be known about the system it describes and is governed by the Schrödinger equation. The Schrödinger equation for a particle of mass m moving in one direction is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$$

where all terms have their usual meanings.

(i) State the Born interpretation of the wavefunction ψ for a one-dimensional system. Show that the wavefunction $\psi = e^{-x^2}$ is square-integrable over the interval $(-\infty, \infty)$ but $\psi = e^{x^2}$ is not.

(15 marks)

(ii) Identify the kinetic energy operator for the system above and briefly discuss the correlation between the kinetic energy of the particle and wavefunction ψ.

(15 marks)

(iii) To find $\psi(x)$ for a free particle $(V(x) = 0)$ confined to a finite region $(0 \leq x \leq a)$ by infinitely high walls, one must solve:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \qquad 0 \leq x \leq a$$

(I) If $\psi(x) = A\cos kx + B\sin kx$ is a solution of the above equation, find k. (A and B are constants.)

(10 marks)

(II) Determine A, B and the energy of the particle E if $\psi(x) = 0$ at the walls $(x = 0, a)$ and also outside the region.

(40 marks)

(III) Briefly discuss how the separation between adjacent energy levels of the particle is affected by mass (m) and length (a)

(10 marks)

(IV) Find the most probable location of the particle in the ground state.

(10 marks)

Useful relations:

$$\int sin^2bx\, dx = \frac{x}{2} - \frac{sin2bx}{4b} + C$$

03 Answer **all** parts.

(a) There are two principal modes of adsorption of molecules on solid surfaces namely, physisorption and chemisorption.

(i) Give four characteristic features to distinguish between them.

(03 x 4 marks)

(ii) Interpret the process of adsorption using thermodynamic viewpoint.

(09 marks)

(b) Surface active agent is a substance that, when dissolved in water, has an ability to remove dirt from surfaces such as the human skin, textiles, and other solids.

(i) Characterize the nature of surfactants that are responsible for their cleansing action.

(10 marks)

(ii) What is meant by the critical micelle concentration (CMC) of a surfactant?

(10 marks)

(iii) Briefly describe two different cleansing mechanisms of surfactants on soiled clothes.

(14 marks)

(c) Capillary action was first recorded by the Italian greatest polymath Leonardo da Vinci.

(i) What is capillary action?

(05 marks)

(ii) Derive the equation for capillary rise or fall that pertains to surface tension of the liquid involved. Consider r and θ as the radius of the capillary tube and the angle measured through the liquid, where a liquid–vapor interface meets a solid surface.

(15 marks)

(iii) Mercury has an angle of contact equal to 140° with soda lime glass. A narrow glass tube of radius 2 mm is dipped in a vessel containing mercury. Calculate the capillary rise of mercury level in the tube.

Note: Surface tension of mercury $\gamma = 0.456$ N m^{-1}; Density of mercury $\rho = 13.6 \times 10^3$ kg m^{-3} and $g = 9.81$ m s^{-2}

(25 marks)

Section B

04. Answer **all** parts.

Astronomers detect the molecules in outer space using radio telescopes based on the signals produced during rotational transitions.

(a) Most of the molecules discovered in the less active regions of the space have linear structures. One of the **largest linear** structures detected was HC_9N.

(i) Draw the structure of this molecule. (Hint: include triple bonds)

(07 marks)

(ii) Determine the number of translational, rotational, and vibrational modes of this molecule.

(08 marks)

(iii) Explain why this molecule is rotationally active.

(05 marks)

(b) Rotational energy levels of a linear molecule are defined by

$$E_J = J(J+1)Bh$$

where J is the rotational quantum number with possible values of 0, 1, 2, ..., B is the rotational constant and h is Planck's constant.

(i) State the main approximation that has been used when deriving this equation. What are the limitations of this approximation?

(10 marks)

(ii) Derive an expression for the frequency of a rotational transition between $J-1$ and J energy levels.

(10 marks)

(c) Two signals have been detected for the HC_9N molecule. One corresponds to the transition between J=28 to J=27 and the other is between J=29 to J=28. The frequency corresponding to the transition between J=28 to J=27 was found as 16268.95 MHz.

(i) Using the above data, calculate the rotational constant of HC_9N.

(10 marks)

(ii) Calculate the frequency corresponding to the transition between J=29 to J=28 levels.

(15 marks)

(d) One of the most abundant heteronuclear diatomic molecules detected in space is carbon monoxide $^{12}C^{16}O$. Masses of the two atoms are 12.000 amu and 15.9994 amu.

(i) Calculate the reduced mass of a molecule of $^{12}C^{16}O$.

(10 marks)

(ii) Given the signal from (J = 1) to (J = 0) for $^{12}C^{16}O$ was observed at 115271.204 MHz, calculate the rotational constant and determine the bond distance of the molecule.

Note: Rotational constant, B for a diatomic molecule is given by $B = \frac{h}{8\pi^2\mu r^2}$ where r is the bond distance, h is the planck's constant and μ is the reduced mass.

(25 marks)

05. Answer **all** parts.

(a) The fundamental vibrational frequency, ν of a diatomic molecule is given by,

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

where k is the force constant and μ is the reduced mass.
Also, the vibrational energies of a such molecule are given by

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

where n is vibrational quantum number with possible values of 0, 1, 2, ...

(i) What is the approximation above equations are based on? Briefly explain.

(10 marks)

(ii) What is the zero-point vibrational energy? Derive an equation for the same.

(07 marks)

(iii) Explain what you mean by fundamental vibrational transitions and overtones using an energy level diagram.

(08 marks)

(b) Isotopic substitution is used to understand the mechanisms of organic reactions. Let hydrogen atom of a C-H bond be substituted by deuterium (D) atom.

(i) Calculate the reduced mass of C-H (CH) and C-D (CD) in atomic mass unit. Assume that the mass of deuterium is twice that of hydrogen.

(10 marks)

(ii) Given that the force constant (k) for C-H stretching is the same as that for the C-D stretching and the C-H stretching wavenumber is 2900 cm^{-1}, find the corresponding C-D stretching wavenumber.

(15 marks)

(iii) Calculate the zero-point vibrational energy of C-H stretching in kJ mol^{-1}

(20 marks)

(c) Raman spectroscopy is based on the inelastic light scattering in a molecule.

(i) Explain Rayleigh scattering, Stokes Raman and anti-Stokes Raman scattering using an energy level diagram.

(10 marks)

(ii) Explain why symmetric stretching mode of CO_2 is Raman active but not IR active.

(10 marks)

(iii) The wavenumber of the incident radiation in a Raman spectrometer is 20623 cm^{-1}. What is the wavenumber of the scattered Stokes radiation for the $J = 4 \leftarrow 2$ transition of $^{16}O_2$?

Note: Rotational constant of $^{16}O_2$ is 1.4457 cm^{-1}

(10 marks)

06. Answer **all** parts.

(a) State the Stark-Einstein law of photochemical equivalence.

(10 marks)

(b) Once excited by ultraviolet light to an electronically excited state, a molecule can undergo a number of photophysical processes.

(i) Giving their general terms, explain briefly the two radiative photophysical processes of an excited state in terms of total spin change.

(10 marks)

(ii) State which process (transition) mentioned above is allowed according to spin selection rule.

(05 marks)

(c) Briefly explain intersystem crossing and chemiluminescence in photochemistry

(20 marks)

(d) If 25% of the energy of a 100 W incandescent bulb generates visible light having average wavelength of 600 nm, how many quanta of light are emitted in 15 min?
(**Note**: 1 W= $1 Js^{-1}$)

(25 marks)

(e) Consider the following reaction series for the photolysis of HI.

$$HI + h\nu \xrightarrow{I_a} H\bullet + I\bullet$$

Rate of photolysis = intensity of absorbed light (I_a)

$$H\bullet + HI \xrightarrow{k_2} H_2 + I\bullet$$

$$I\bullet + I\bullet \xrightarrow{k_3} I_2$$

Using the above mechanism, derive expressions for the following.

(i) Rate of disappearance of HI
(ii) Rate of formation of H•
(iii) Find the relationship between the rate of decomposition of HI and the intensity of the absorbed light (I_a). What is the assumption you have made when deriving the above relationship?
(iv) Calculate the quantum yield for the disappearance of HI (Φ_{HI}).

(30 marks)

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