(2½ Hours) [Total Marks : 60

N.B. : (1) **All** questions are **compulsory.**
(2) **Figures** to the **right** indicate **maximum marks.**
(3) Use of **Non-programmable** scientific **calculator** is **allowed.**

Useful constants :

c	$= 2.998 \times 10^{8}$ ms^{-1}	e	$= 1.602 \times 10^{-19}$ C
R	$= 8.314$ J K^{-1} mol^{-1}	k	$= 1.3811 \times 10^{-23}$ J K^{-1}
h	$= 6.625 \times 10^{-34}$ Js	1 J	$= 6.24 \times 10^{18}$ eV
m_e	$= 9.109 \times 10^{-31}$ kg	1 eV	$= 8.06 \times 10^{3}$ cm^{-1}
N_A	$= 6.023 \times 10^{23}$ mol^{-1}	1amu	$= 1.66 \times 10^{-27}$ kg

Atomic Mass of C = 12, O = 16.

1. (a) Attempt **any two** of the following :

(i) Explain the terms : **4**
(1) Linear operator
(2) Hermitian operator

(ii) Formulate the Schrödinger wave equation for a particle in one dimensional box and obtain the normalised wave function for it. **4**

(iii) Show that the functions : **4**

$$\psi_1 = \left(\frac{1}{2\pi}\right)^{1/2}$$

$$\psi_2 = \left(\frac{1}{\pi}\right)^{2} \cos x$$

$$\psi_3 = \left(\frac{1}{\pi}\right)^{2} \sin x$$

in the interval $x = 0$ to $x = 2\pi$ are orthogonal to each other.

(iv) What is linear harmonic oscillator? Obtain an expression for linear harmonic oscillator from the following equation. **4**

$$\frac{d^2\psi}{dy^2} + \left(\frac{\alpha}{\beta} - y^2\right)\psi = 0$$

TURN OVER

(b) Attempt **any one** of the following :

(i) If $\hat{A} = 3x^2$ and $\hat{B} = \frac{d}{dx}$ then show that $\hat{A}$ and $\hat{B}$ do not commute. 4

(ii) A particle of mass 'm' is confined in one dimensional box of length 'a'. Calculate the probability of finding the particle at x where $0 \leq x \leq a/4$. 4

2. (a) Attempt **any two** of the following :

(i) Obtain the equations of separation of variables from the Schrödinger wave equation in terms of spherical coordinates. 4

(ii) Explain the need for approximate solution to two electron system. Show how the problem of two electron system can be reduced to problem of one electron system. 4

(iii) What are radial probability distribution curves? Qualitatively plot the radial probability distribution curves for 3s, 3p and 3d orbital's. 4

(iv) With respect to hydrogen like atom, answer the following : 4

(1) Write the Hamiltonian operator for it and identify the terms involved.

(2) Mathematically express the coordinates of the centre of mass and relative coordinates of the system.

(b) Attempt **any one** of the following :

(i) The internuclear distance between carbon and oxygen atom in carbon monoxide molecule, which acts as a rigid rotor, is 1.13×10^{-10} m. What is the rotational energy for J = 3? 4

(ii) A hydrogen like orbital is given below : 4

$$\psi = \frac{\sqrt{2}}{81\sqrt{\pi}} Z^{3/2} \cdot (6 - Zr)\, Zre^{-Zr/3} \cdot \cos\theta \text{ (in a.u.)}$$

Determine the quantum numbers n, l and m by inspection and identify the orbital.

TURN OVER

3. (a) Attempt **any two** of the following :

(i) On the basis of the collision theory, derive an expression for the rate constant of a bimolecular gaseous reaction. **4**

(ii) Define kinetic chain length and show that the rate of polymerization reaction is proportional to the square root of the initiator concentration. **4**

(iii) Explain the variation of the rate of reaction with pressure and the three explosion limits in the reaction between H_2 and O_2. **4**

(iv) For the thermal decomposition of acetaldehyde, show that **4**

$$\frac{d}{dt}[CH_4] = k[CH_3CHO]^{3/2}$$

(b) Attempt **any one** of the following :

(i) On the top of a certain mountain, the atmospheric pressure is 530 mm Hg and the pure water boils at 360 K. A climber finds that it takes 300 minutes to boil an egg as against 3 minutes at 370 K. **4**

(1) What is the ratio of the rate constant k_{370} / k_{360}?

(2) Calculate the energy of activation for the reaction that occurs when the egg is boiled assuming that the pre-exponential factor A remains constant.

(ii) Consider the following consecutive reaction : **4**

$$R_1 \xrightarrow{k_1} R_2 \xrightarrow{k_2} R_3.$$

where k_1 and k_2 are the rate constants for a first order reaction. If $k_1 : k_2 = 1.0 : 0.15$ and $k_1 = 4.0 \times 10^{-2}$ min^{-1}, then calculate the time required for the concentration of R_2 to reach a maximum.

4. (a) Attempt **any two** of the following :

(i) Derive an expression for the kinetics of reactions in the solid state for spherical particles. **4**

(ii) Derive an expression for the rate law of kinetics of reactions in solid state. **4**

(iii) Discuss with mathematical expression the enzyme inhibition by competitive method. **4**

(iv) Using Michaelis - Menten equation show both graphically and mathematically, how the rate and order of an enzyme catalysed reaction depends on the concentration of the substrate. 4

(b) Attempt **any one** of the following :

(i) Derive Hammett equation of linear free energy relationship. 4

(ii) Derive an expression to show the effect of solvent dielectric constant on ionic reactions. 4

5. Attempt **any four** of the following : 12

(a) State Heisenberg's uncertainty principle. An electron moves in the first orbit with a speed of 2×10^6 ms^{-1}. If its momentum is measured with an accuracy of 1%, what is the uncertainty of position?

(b) Find the eigen function and eigen value of the linear momentum operator

$$\frac{h}{2\pi i}\frac{d}{dx}.$$

(c) Write the expression for potential energy of hydrogen like system. Why is it characterised by spherically symmetrical potential energy?

(d) How will you express the cartesian coordinates in terms of polar coordinates? Explain with a suitable diagram.

(e) Explain the principle of microscopic reversibility.

(f) Explain in brief the Rice-Ramsperger-Kassel-Marcus (RRKM) theory.

(g) Give a general account of enzyme action.

(h) Predict the effect of increase in ionic strength on the rate constant for each of the following reactions :

(i) $Co(NH_3)_5Br^{2+} + Hg^{2+} \rightarrow$ Products

(ii) $S_2O_8^{2-} + I^- \rightarrow$ Products

(iii) $C_{12}H_{22}O_{11} + OH^- \rightarrow$ Products
