(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 = $2{\cdot}998 \times 10^{8}$ ms^{-1}		**k** = $1{\cdot}3811 \times 10^{-23}$ JK^{-1}	
R = $8{\cdot}314$ JK^{-1} mol^{-1}		**1 J** = $6{\cdot}24 \times 10^{18}$ eV	
h = $6{\cdot}625 \times 10^{-34}$ Js		**1 eV** = $8{\cdot}06 \times 10^{3}$ cm^{-1}	
m_e = $9{\cdot}110 \times 10^{-31}$ kg		**1 amu** = $1{\cdot}66 \times 10^{-27}$ kg	
N_A = $6{\cdot}023 \times 10^{23}$ mol^{-1}		**C** = 12	
e = $1{\cdot}602 \times 10^{-19}$ C		**O** = 16	

(a) Attempt any **two** of the following :—

(i) What is photo electric effect ? Explain how it brings out the particulate nature of light. **4**

(ii) Prove – eigen functions of Hermitian operator belonging to different eigen values are necessarily orthogonal. **4**

(iii) For Hermite's differential equation **4**

$$\frac{d^2F}{dy^2} - 2y\frac{dF}{dy} + \left(\frac{\alpha}{\beta} - 1\right)F = 0$$

obtain the recursion formula.

(iv) Starting with equation $\left(\frac{\partial^2 \psi}{\partial x^2}\right)_t = \frac{1}{v^2}\left(\frac{\partial^2 \psi}{\partial t^2}\right)_x$ **4**

set up time independent Schrodinger wave equation.

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

(i) Which of the following functions are eigen functions of the operator **4**

$\frac{d}{dx}$: e^{-4x}, e^{-4x^2}, e^{ikx} and e^{-ax^2} ? Give eigen value for eigen function.

(ii) Calculate the spacing between lowest and next higher energy level for particle **4**
'A' (mass = 10^{-30} kg) in one dimensional box of length 10^{-10} m and particle 'B' of mass 10^{-3} kg in one dimensional box of length 10 cm. State giving reason for which particle quantisation is observed.

[TURN OVER

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

(i) Explain the term 'Spherical Harmonics'. 4

(ii) Obtain the radial wave equation for hydrogen atom from the following Schrodinger wave equation in spherical coordinates.

$$-\frac{h^2}{8\pi^2 m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi$$

$$-\frac{ze^2}{r}\psi = E\psi.$$

(iii) Discuss the angular probability distribution for p-orbitals. 4

(iv) Explain the 'independent electron approximation' as applied to two electron system. 4

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

(i) Consider CO molecule as rigid rotor, the internuclear distance is $1{\cdot}131 \times 10^{-10}$m. Calculate the rotational energy for J = 2. 4

(ii) Find the most probable distance of the electron from the nucleus of hydrogen atom in 1s and 2s states. 4

(a) Attempt any **two** of the following :—

(i) Obtain the rate law expression for thermal reaction $H_2 + Br_2 \rightarrow 2HBr$. 4

(ii) Discuss the gas phase combustion reaction between hydrogen and oxygen and explain explosion limit and factors affecting explosion limit. 4

(iii) Explain the kinetics of free radical chain polymerisation. 4

(iv) Explain Rice-Ramsperger-Kassel-Marcus theory. 4

(b) Attempt any one of the following :—

(i) In a bimolecular reaction the energy of activation is 180 kJ mol^{-1} at 550 K. Calculate the specific reaction rate of reaction at 550 K. The number of molecules colliding per cubic centimeter per second is 6×10^{31}. 4

(ii) The energy of activation for a bimolecular reaction is 82 kJ mol^{-1}. Calculate the fraction of molecules having sufficient energy to react at 500 K. 4

(a) Attempt any two of the following :—

(i) Discuss the kinetics of enzyme inhibition by uncompetitive inhibition method. 4

(ii) Discuss the kinetics of regulatory enzymes with the help of Hill equation. 4

(iii) Derive an expression for contracting area rate law. 4

(iv) Derive the parabolic rate law of kinetics of reactions in solid state. 4

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

(i) Derive an expression to show the influence of ionic strength on rates of the reaction between ions. **4**

(ii) Give an account of effects of solvent polarity on rates of reaction in solution. **4**

Attempt any **four** of the following :— **12**

(a) Give the expression for allowed energy levels of linear harmonic oscillator. Comment on spacings of energy levels. What is zero point energy ?

(b) Find the degenerate and non-degenerate energy levels for a cubical box from the following :—

$$E = \frac{6h^2}{8ma^2}, \quad E = \frac{9h^2}{8ma^2}, \text{ and } \quad E = \frac{12\,h^2}{8\,ma^2}$$

(c) What information is obtained by radial probability distribution curves ? Sketch qualitatively the radial distribution curves for 1s, 2s and 2p.

(d) Transform cartesian coordinates (x, y, z) into polar coordinates (r, θ, ϕ). Identify r, θ, ϕ.

(e) Explain consecutive reactions with examples.

(f) Explain the terms :—

(i) Collision frequency

(ii) Steric factor.

(g) Why enzyme catalysed reactions are temperature and pH sensitive ? Show the effect of the same graphically.

(h) Discuss the effect of solvent cohesion energy on rates of reaction in solution.