(2½ Hours) **[Total Marks : 60**

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

Useful constants :

$c = 2.998 \times 10^{8}\ ms^{-1}$
$R = 8.314 \times JK^{-1}\ mol^{-1}$
$h = 6.626 \times 10^{-34}\ Js$
$m_e = 9.109 \times 10^{-31}\ kg$
$N_A = 6.022 \times 10^{23}\ mol^{-1}$
$e = 1.602 \times 10^{-19}\ C$
$k = 1.3811 \times 10^{-23}\ JK^{-1}$
$1J = 6.24 \times 10^{-18}\ eV$
$1\ eV = 8.06 \times 10^{3}\ cm^{-1}$
$1\ amu = 1.66 \times 10^{-27} kg$
$1atm = 1.013 \times 10^{5}\ Nm^{-2}$

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

(i) What is Hermitian operator ? Show that if two operators $\hat{A}$ and $\hat{B}$ are Hermitian, then their product $(\hat{A}\hat{B})$ is also Hermitian, if $\hat{A}$ and $\hat{B}$ commute with each other. **4**

(ii) What is zero point energy ? Show that the energy of a particle in a one dimensional box of length 'a' is given by the expression $E_n = \frac{n^2h^2}{8ma^2}$. **4**

(iii) Explain the term 'expectation values'. Find the expectation value of position operator $\bar{x}$ in a one dimensional box of length L, if $\psi = \sin\frac{n\pi x}{L}$ is normalised and a real function. **4**

(iv) Derive the Hermites differential from the relation $\frac{d^2\psi}{dy^2} + \left(\frac{\alpha}{\beta} - y^2\right)\psi = 0$. **4**

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

(i) Which of the following functions are eigen function for the operator $\frac{d^2}{dx^2}$. **4**
(P) $6\sin 5x$ (q) $4e^{-5x}$
Find the eigen value in each case.

(ii) The function given below are defined in the interval x = -a to x = +a **4**
(p) $\psi_{1(x)} = N_1 (a^2 - x^2)$ (q) $\psi_{2(x)} = N_2\ x(a^2 - x^2)$
Assuming the functions to be zero for x < -a and x > a, find the values of the normatisation constants N_1 and N_2.

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

(i) Explain the variation method for obtaining approximate solution of Schrodinger wave equation. **4**

(ii) Obtain an expression for Hamiltonian operator for a rigid rotor in spherical coordintes. **4**

(iii) The Schrodinger equation for a two particle system is given by **4**

$$\left[-\frac{h^2}{8\pi^2(M+m)}\nabla_q^2-\frac{h^2}{8\pi^2\mu}\nabla_r^2-\frac{Ze^2}{4\pi\varepsilon_0 r}\right]\psi_{T(q,r)}=E_T\psi_{T\ (q,r)}$$

obtain the Schrodinger wave equation for translational motion and Internal motion separately from the above equation.

(iv) On the basis of angular probability distribution curves, explain the shapes of 'p' orbital. **4**

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

(i) Calculate the most probable distance of an electron from the nucleus in ground state of hydrogen atom. The normalised ground state function is **4**

$$\psi_{1s}=\frac{1}{\sqrt{\pi}\,a_0^{3/2}}\,e^{\frac{-r}{a_0}}$$

(ii) Calculate the values of first two rotational energy levels of a rigid rotor, whose moment of inertia is 1.457×10^{-46} m^2. **4**

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

(i) Explain the Rice-Ramsperger-Kassel - Marcus (RRKM) theory. **4**

(ii) Show that the rate of polymerization reaction is proportional to the square root of its initiator concentration. **4**

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

(iv) Using the steady state approximation for the thermal decomposition of acetaldehyde show that $\frac{d}{dt}[CH_4]=k[CH_3CHO]^{3/2}$. **4**

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

(i) The energy of activation for the dissociation of HI is 184.2 $kJmol^{-1}$. The number of molecules colliding per cubic centimeter per sec is 6×10^{31} a 556K. Calculate the specific reaction rate in mol dm^{-3} s^{-1} at 556 K. **4**

(ii) The following process are the first order kinetics **4**

$x \xrightarrow{22.3\ d} y \xrightarrow{33.2\ d} z$ where the times are the half lives of the reactions in days. At what stage of time will the concentration of y become maximum ?

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4. (a) Attempt any **two** of the following :–
   (i) Derive an expression for the first order rate law of kinetics of reactions in solid state **4**
   (ii) Derive kinetic expression for the contracting sphere rate law of reactions in solid state. **4**
   (iii) Discuss the noncompetitive inhibition of enzyme catalysis. **4**
   (iv) Derive kinetic expression of Michaelis-Menten equation of enzyme catalysed reaction. **4**

   (b) Attempt any **one** of the following :–
   (i) Derive an expression to show the influence of ionic strength on the rates of ionic reactions. **4**
   (ii) Derive Hammett equation of linear free energy relationship. **4**

5. Attempt any **four** of the following :– **12**
   (a) State the postulates of quantum mechanics.
   (b) What is probability density ? Sketch the plot of probability density for n=2 and n=3.
   (c) Write only the expressions for total wave function for 1s, 2s and 2p orbitals of hydrogen atom.
   (d) Explain the significance of magnetic quantum number.
   (e) Explain the principle of microscopic reversibility.
   (f) Explain the terms : (i) collision frequency factor and (ii) reaction cross section.
   (g) Discuss the factors which affect the reactions in solids.
   (h) How should the following reactions depend on the ionic strength of the reaction medium ?
   (i) $[Pt\ (NH_3)_3Br]^+ + CN^- \rightarrow$ Products
   (ii) $[Pt\ Cl_4]^{2-} + CN^- \rightarrow$ Products
   (iii) $[Pt\ (NH_3)_2Cl_2] + Cl^- \rightarrow$ Products

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