QP Code : 13827

(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}

$R = 8{\cdot}314$ JK^{-1} mol^{-1}

$h = 6{\cdot}625 \times 10^{-34}$ Js

$m_e = 9{\cdot}110 \times 10^{-31}$ kg

$N_A = 6{\cdot}023 \times 10^{23}$ mol^{-1}

$e = 1{\cdot}602 \times 10^{-19}$ C

$k = 1{\cdot}3811 \times 10^{-23}$ JK^{-1}

lJ = $6{\cdot}24 \times 10^{18}$ eV

leV = $8{\cdot}06 \times 10^{3}$ cm^{-1}

lamu = $1{\cdot}66 \times 10^{-27}$ kg

H = 14

I = 16.

1. (a) Attempt any **two** of the following :–
   (i) Set up the Schrodinger wave equation for a particle in three dimensional box. Using the method of separation of variables, show that it can be expressed as three equations containing one variable each. **4**
   (ii) Explain the term 'expectation value' of a dynamical quantity. **4**
   (iii) Explain with the help of suitable example the term 'eigen value equation.' Show that eigen values of Hermitian operator are real. **4**
   (iv) What are operators ? Why they are important in quantum mechanics ? How linear momentum operator $\hat{p}_x$ is derived ? **4**

   (b) Attempt any **one** of the following :–
   (i) The Hermite polynomials are obtained from the generating functions :– **4**

$$H_n(y) = (-1)^n \; e^{y^2} \; \frac{d^n}{dy^n}\left(e^{y^{-2}}\right)$$

   Calculate the polynomial for n = 2, 3.
   (ii) An electron is confined in a cubical box 1·00 nm in length breadth and height. Find the energy eigen values of the first two energy levels in eV. **4**

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

(i) For a particle rotating in three dimensions, write the Hamiltonian for it in terms of cartesian coordinates (x, y, z). With the help of diagram only, show the transformation of cartesian coordinates into polar coordinates (r, ϕ, θ). Give x, y, z in terms of appropriate r, θ and ϕ. Write the Schrodinger wave equation in polar coordinates. 4

(ii) The Schrodinger equation for two particle system is :– 4

$$\left[-\frac{h^2}{8\pi^2(M+m)}.\nabla^2_q - \frac{h^2}{8\pi^2\mu}\nabla^2_r - \frac{Ze^2}{4\pi\varepsilon_0 r}\right]\psi_T(q,r) = E_T\,\psi_T(q,r).$$

From the above, obtain the Schrodinger equation for translational motion and internal motion separately.

(iii) Write the Hamiltonian operator for two electron system and identify the kinetic energy and potential energy operators. If $\hat{H}(1)$ operator on electron 1 and $\hat{H}(2)$ operates on electron 2, ϕ represents orbital eigen function and E represents orbital energy eigen value, find the expression for $\hat{H}^o\psi$, $\hat{H}^o$ is zero order Hamiltonian. 4

(iv) Separate the following Schrodinger equation into three ordinary differential equations :– 4

$$-\frac{h^2}{8\pi^2 m}\left[P.F\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + R.F\frac{1}{r^2\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dP}{d\theta}\right) + R.P.\frac{1}{r^2\sin^2\theta}\frac{d^2F}{d\phi^2}\right]$$

$$-\frac{Ze^2}{4\pi\varepsilon_0 r}\cdot RPF = ERPF.$$

Taking into account that $\psi = \psi(r, \theta, \phi) = R(r).P(\theta).F(\phi)$ and R, P and F have been written for R(r), $P(\theta)$ and $F(\phi)$.

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

(i) Calculate the energy of the third rotational energy level in the molecule of NO. The internuclear distance in the molecule is 0·11 nm. 4

(ii) The radial wave function of 2s orbital of a hydrogen atom is given by – 4

$$R_{20} = N\left(Z - \frac{r}{a_0}\right)e^{\frac{-r}{2a_0}} \quad \text{N is a constant.}$$

(1) Qualitatively sketch the radial distribution curve

(2) Determine the distance of node from the nucleus in terms of a_0.

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

(i) Derive expression for the rate constant of a bimolecular gaseous reaction on the basis of collision theory. Explain how it accounts for specific orientation of the reactant molecules. 4

(ii) Define kinetic chain length and show that in chain polymerisation, smaller the initiator concentration greater is the kinetic chain length. 4

(iii) Discuss the various factors affecting the rate of a non-stationary chain reaction and occurence of three explosion limits using suitable mechanism. 4

(iv) Proposed mechanism for thermal decomposition of acetaldehyde is, 4

$$CH_3CHO \xrightarrow{k_1} \cdot CH_3 + \cdot CHO$$

$$\cdot CH_3 + CH_3CHO \xrightarrow{k_2} \cdot CH_4 + \cdot CH_2CHO$$

$$\cdot CH_2CHO \xrightarrow{k_3} \cdot CH_3 + CO$$

$$\cdot CH_3 + \cdot CH_3 \xrightarrow{k_4} CH_3CH_3$$

Show that $\frac{d[CH_4]}{dt} = K[CH_3CHO]^{3/2}$.

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

(i) The rate law for the reaction, $A + 3B \rightarrow C + 2D$ was reported as $\frac{d[c]}{dt} = K.[A][B][C]^{-1}$. Express the rate law in terms of reaction rates. What is the unit of K ? 4

(ii) For the following consecutive reaction, 4

$A \xrightarrow{k_1} B \xrightarrow{k_2} C$

the value of $k_1 = 5{\cdot}65 \times 10^{-3}\ min^{-1}$ and the time necessary to reach the maximum concentration of B is 26 minutes. What is the value of k_2 ?

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

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

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

(iii) On the basis of Michaelis–Menten mechanism show that the rate and order of an enzyme catalysed reaction depend on the concentration of the substrate. 4

(iv) Derive an expression for first order rate law of kinetics of reactions in solid state. 4

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

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

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

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

(a) Differentiate between matter waves and electromagnetic radiations. Show that the wave property and particle property for a photon are corelated.

(b) Give a suitable set of quantum numbers (n_x, n_y, n_z) such that it leads to six fold degeneracy in a cubical box. Also state the corresponding energy value.

(c) Explain – there is an equal chance of finding the 1s electron in any direction with respect to nucleus.

(d) From the following, evaluate the total energy of an orbital of hydrogen atom.

$$\alpha^2 = \frac{8\pi^2 mE}{h^2}, \ \lambda = \frac{4\pi^2 mZe^2}{h^2 \alpha}.$$

(e) Explain the principle of microscopic reversibility.

(f) Explain the limitation of Lindemann theory of unimolecular reactions and how is it accounted for by RRKM theory.

(g) An enzyme catalysed reaction ($K_m = 4{\cdot}3 \times 10^{-3}$ mol dm^{-3}) is inhibited by a competitive inhibitor I ($K_I = 6{\cdot}2 \times 10^{-5}$ mole dm^{-3}). Suppose the substrate concentration is $4{\cdot}1 \times 10^{-4}$ mol dm^{-3}. How much of the inhibitor is needed for a 60% inhibition ?

(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.

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