QP Code : BV-15.

(2½ Hours) [Total Marks :

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 :–

$c = 2{\cdot}998 \times 10^{8}\ ms^{-1}$

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

$h = 6{\cdot}626 \times 10^{-34}\ Js$

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

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

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

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

$1J = 6{\cdot}24 \times 10^{18}\ eV$

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

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

$N = 14$

$O = 16.$

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

(i) State the Heisenbergs Uncertainty Principle. Explain "Uncertainty is not due to any lack of precision in measurement but due to inherent nature (wave particle duality) of the particle." **4**

(ii) What is meant by eigen function ? Show that eigen function of Hermitian operator corresponding to different eigen values are orthogonal. **4**

(iii) Give the expression for energy of a particle in one dimensional box. Explain how does it give rise to concept of quantisation. Plot ψ^2 v/s x for n = 1, 2, 3, 4 and state the number of nodes in each case. **4**

(iv) Obtain the Hermite's differential equation for linear harmonic oscillator from the following equation :– **4**

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

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

(i) Calculate the lowest kinetic energy for an electron in a three dimensional box of dimension 0·001 pm, 0·0015 pm and 0·002 pm. 4

(ii) $\hat{A} = \frac{d}{dx}, \hat{B} = \frac{d^2}{dx^2}$ and $f(x) = \sin x$. 4

Show explicitly whether $\hat{A}$ and $\hat{B}$ are commutative or non-commutative. What does it mean when two operators are said to be non-commutative ?

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

(i) Separate the following Schrodinger equation into two equations each with a single variable in it. 4

$$\frac{\partial^2\psi}{\partial\theta^2} + \frac{\cos\theta}{\sin\theta}\frac{\partial\psi}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2 mr^2}{h^2}E\psi = 0 \text{ where } \psi \text{ is } \psi(\theta,\phi).$$

(ii) Explain why hydrogen like atoms represent a two particle problem. Write the Hamiltonian operator for it. What are "coordinates of centre of mass" and "relative coordinates" ? Why are they necessary ? 4

(iii) With the help of suitable diagram bring out the relationship between cartesian coordinates (x, y, z) and polar coordinates (r,θ,ϕ). Give the limits of variation for x, y, z, r, θ and ϕ. 4

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

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

(i) Calculate the energy of the second rotational energy level J = 2 in the molecule of NO having 110 pm inter nuclear distance. 4

(ii) The energy of hydrogen atom depends on collection of–charge on electron, reduced mass of hydrogen atom ($9{\cdot}104 \times 10^{-31}$ kg), permittivity of free space $\epsilon_0 = 8{\cdot}854 \times 10^{-12}\ C^2/J\ m$, Plancks constant and integer 'n'. 4

If $\frac{C^4\ kg}{8\,(C^2/Jm)^2\,(Js)^2} \times \frac{1}{n^2} = E$.

Calculate 'E' for n = 1 and 2.

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

(i) Explain why the observed rates of bimolecular gaseous reactions are much lower than that predicted by collision theory ? 4

(ii) Discuss the effect of initiator concentration on the rate of free radical chain polymerisation. 4

(iii) Describe the effect of pressure and temperature on the rate of an explosion reaction with the help of a suitable example. 4

(iv) Consider the following mechanism for thermal decomposition of R_2, 4

$$\text{(i)}\ R_2 \xrightarrow{k_1} 2R\cdot$$

$$\text{(ii)}\ R\cdot + R_2 \xrightarrow{k_2} P_B + R\cdot'$$

$$\text{(iii)}\ R\cdot' \xrightarrow{k_3} P_A + R\cdot$$

$$\text{(iv)}\ 2R\cdot \xrightarrow{k_4} P_A + P_B$$

Where P_A, P_B and R_2 are stable hydrocarbons and R· and R·' are radicals. Find the rate of decomposition of R_2. Comment on the effect of concentration of R_2 on the rate of reaction.

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

(i) The rate of formation of C in the reaction, 4
$2A + B \rightarrow 2C + 3D$ is 1 mol L^{-1} s^{-1}. State the reaction rate and the rates of formation or consumption of A, B and D.

(ii) The following process follows first order kinetics, 4
$x \xrightarrow{22.5\,d} y \xrightarrow{33.0\,d} z$. The times are half lives in days. At what stage will the concentration of y be maximum ?

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

(i) Derive an expression to show the effect of dielectric constant on rates of reaction between ions in solution. 4

(ii) Discuss Lineweaver-Burk and Eadie-Hoftsee plot for analyzing rate data of enzyme catalysed reactions. 4

(iii) Discuss the kinetics of enzyme inhibition by competitive inhibition method. 4

(iv) Derive an expression for the parabolic rate law for reactions in solids. 4

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

(i) Show how contracting area rate law helps in determining order of solid state reaction interms of volume of the material present. 4

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

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

(a) Show how linear momentum operator $\hat{p}_x$ is derived.

(b) Give the characteristics of a free particle. Write the Schrodinger equation for it.

(c) Compare the radial probability distribution curves for 1s, 2s and 2p orbitals.

(d) Write the complete wave function of hydrogen like atoms. Give the significance of principle quantum number.

(e) Deduce the mechanism for unimolecular reactions and derive an expression for the rate constant of an unimolecular reaction.

(f) Derive the rate law for the decomposition of ozone in the reaction $2O_{3(g)} \rightarrow 3\ O_{2(g)}$ on the basis of the following mechanism, using steady state approximation.

$$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O$$

$$O + O_3 \xrightarrow{k_2} 2\,O_2 \text{ (slow)}$$

(g) Calculate the concentration of a non-competitive inhibitor , [$K_I = 3{\cdot}5 \times 10^{-4}$ moldm^{-3}) needed to yield 75% inhibition of an enzyme catalysed reaction.

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

(i) $Pt(NH_3)_3 Cl^+ + NO_2^- \rightarrow$ Products

(ii) $PtCl_4^{2-} + OH^- \rightarrow$ Products

(iii) $Pt(NH_3)_2 Cl_2 + OH^- \rightarrow$ Products.

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