

- 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 :-

$$c = 2.998 \times 10^8 \text{ ms}^{-1}$$

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$h = 6.626 \times 10^{-34} \text{ Js}$$

$$m_e = 9.110 \times 10^{-31} \text{ kg}$$

$$N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$$

$$e = 1.602 \times 10^{-19} \text{ C}$$

$$k = 1.3811 \times 10^{-23} \text{ JK}^{-1}$$

$$h\nu = 6.24 \times 10^{18} \text{ eV}$$

$$1 \text{ eV} = 8.06 \times 10^3 \text{ cm}^{-1}$$

$$1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg}$$

$$N = 14$$

$$O = 16.$$

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

- (i) State the Heisenberg's 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

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

(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

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

(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

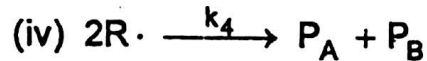
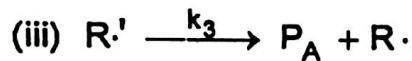
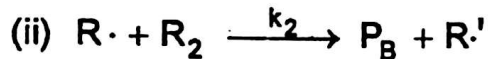
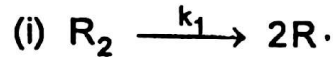
(ii) The energy of hydrogen atom depends on collection of-charge on electron, reduced mass of hydrogen atom (9.104×10^{-31} kg), permittivity of free space $\epsilon_0 = 8.854 \times 10^{-12}$ C²/J m, Plancks constant and integer 'n'. 4

$$\text{If } \frac{C^4 \text{ kg}}{8 (C^2 / J m)^2 (J s)^2} \times \frac{1}{n^2} = E$$

Calculate 'E' for n = 1 and 2.

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



Where P_A , P_B and R_2 are stable hydrocarbons and $R\cdot$ and $R\cdot'$ 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, $2A + B \rightarrow 2C + 3D$ is $1 \text{ mol L}^{-1} \text{ s}^{-1}$. State the reaction rate and the rates of formation or consumption of A, B and D. 4

- (ii) The following process follows first order kinetics, 4
- $$x \xrightarrow{22.5d} y \xrightarrow{33.0d} z$$
- 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-Hofstee 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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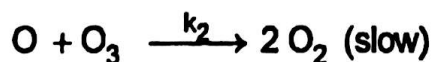
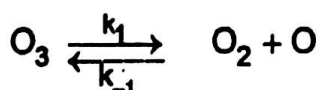
(b) Attempt any one of the following :-

- (i) Show how contracting area rate law helps in determining order of solid state reaction in terms 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 $2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g})$ on the basis of the following mechanism, using steady state approximation.



- (g) Calculate the concentration of a non-competitive inhibitor, $[K_I = 3.5 \times 10^{-4} \text{ mol dm}^{-3}]$ 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) $\text{Pt}(\text{NH}_3)_3 \text{Cl}^+ + \text{NO}_2^- \rightarrow \text{Products}$
- (ii) $\text{PtCl}_4^{2-} + \text{OH}^- \rightarrow \text{Products}$
- (iii) $\text{Pt}(\text{NH}_3)_2 \text{Cl}_2 + \text{OH}^- \rightarrow \text{Products}$.