

2026

CHEMISTRY — HONOURS

Paper : DSCC-13

(Physical Chemistry - IV)

Full Marks : 75

*The figures in the margin indicate full marks.**Candidates are required to give their answers in their own words as far as practicable.*Answer **question nos. 1, 2, 3, 4 (compulsory)** and **any four** questions from the rest (**question nos. 5 to 10**).1. Answer **any ten** questions :

2×10

- (a) Find out the average amplitude of oscillation
- $\langle x \rangle$
- of a harmonic oscillator in its ground state.

$$\text{Given, } \psi_0 = \left(\frac{\alpha}{\pi} \right)^{\frac{1}{4}} e^{-\frac{\alpha x^2}{2}}.$$

- (b) Characterise and differentiate between overtones and hot bands in IR spectra.
- (c) What is the difference between 'Activated Complex' and a 'reaction intermediate'?
- (d) What are the necessities for approximation methods in quantum mechanics? State the linear variation principle.
- (e) If the $J = 2$ to $J = 3$ rotational transition for a heteronuclear diatomic molecule occurs at $\lambda = 20$ nm, find the wave number for transition from $J = 5$ to $J = 6$ level in the same molecule.
- (f) Write down the Schrödinger equation for 'He' atom clearly mentioning the terms involved.
- (g) "The nature of Raman spectrum of a substance depends on both the nature of molecules and the wavelength of incident radiation"—justify or criticize.
- (h) Does the rate of photochemical reaction depends on temperature? Explain.
- (i) "2s and 2p orbitals of Hydrogen atom have same energy"—justify or criticize.
- (j) Write the correct order of the fundamental vibration frequencies of the following diatomic molecules : H^1Cl^{35} , D^2Cl^{35} , H^1Cl^{37} .
- (k) "For the reaction in aqueous medium $\text{S}_2\text{O}_8^{2-} + \text{I}^- \rightarrow \text{pdts}$, the rate constant increases in presence of KCl at a certain temperature"—justify or criticize.
- (l) Draw the radial distribution curve of 2p orbital of Hydrogen atom clearly mentioning the two axes.

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2. (a) Write short notes on one-dimensional simple harmonic oscillator covering the following points :

- (i) Schrödinger equation indicating the potential energy expression.
- (ii) Energy expression, potential energy diagram showing energy levels and existence of zero point energy with explanation.
- (iii) Drawing of wave functions for $v = 0$ and $v = 1$ levels. 1+3+1

Or

(b) Write short notes on Hydrogen atom covering the following points :

- (i) Schrödinger equation in spherical polar coordinate
- (ii) Separation of variables (r, θ, ϕ)
- (iii) Solution of the ϕ part. 1+3+1

3. (a) Write short notes on Raman effect covering the following points :

- (i) Description with proper diagram.
- (ii) Intensity distribution of the spectral lines with explanation.
- (iii) Selection rules for rotational and vibrational Raman spectroscopy. 2+2+1

Or

(b) Write short notes on electronic spectroscopy covering the following points :

- (i) Potential energy diagram showing fluorescence and phosphorescence.
- (ii) Differentiation between fluorescence and phosphorescence on the basis of time scale, frequency and intensity. 2+3

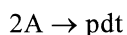
4. (a) Write short notes on quantum yield of a photochemical reaction covering the following points :

- (i) Definition
- (ii) Reasons behind low and high quantum yield with examples.
- (iii) Principle of determination of quantum yield of a photo-chemical reaction using chemical-actinometer. 1+2+2

Or

(b) Write short notes on collision theory of reaction rate covering the following points :

- (i) Assumptions
- (ii) Derivation of expression of rate constant for the bi-molecular second order gas phase reaction :



- (iii) Limitations. 1+3+1

5. (a) Express $\widehat{L}_x$, $\widehat{L}_y$ and $\widehat{L}_z$ in spherical polar coordinate and hence, show that.

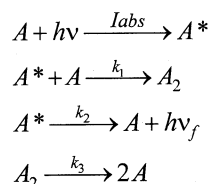
$$[\widehat{L}_x, \widehat{L}_y] = i\hbar \widehat{L}_z$$

- (b) Discuss the effect on anharmonicity on the vibrational spectra of a heteronuclear di-atomic molecule.
- (c) Molar extinction coefficient is the reciprocal of the thickness of the solution, when the intensity of the incident radiation falls to $\frac{1}{10}$ of its initial value. Determine whether it is true or false with proper explanation. 4+3+3
6. (a) The first rotational absorption is found at 3.8424 cm^{-1} for $^{12}\text{C}^{16}\text{O}$ while that of $^{13}\text{C}^{16}\text{O}$ is found to occur at 3.6734 cm^{-1} . Assuming molar masses of ^{16}O and ^{12}C as 15.9994 gm/mol and 12.000 gm/mole respectively. Calculate the molar mass of ^{13}C .
- (b) Explain the concept of potential energy surface. What is saddle point?
- (c) For a particle in an infinitely deep one-dimensional potential box of length L , apply the trial wave function : $\psi = N \cdot x \cdot (L^2 - x^2)$, [L is the length of the 1D-box] to calculate the energy. Which wave function does this wave function approximate to? 4+3+3
7. (a) Derive the Michaelis-Menten equation of enzyme catalysis and draw the Lineweaver-Burk plot showing slope and intercept.
- (b) Find out the probability of finding the 1s electron in the first Bohr orbit and at a distance of $1 \times 10^{-4} a_0$ from the nucleus. Comment on the result.
- (c) The fundamental and first overtone transitions of a molecule AB are found to occur at 1880.01 cm^{-1} and 3824.00 cm^{-1} respectively. Evaluate $\bar{\nu}_e$, x_e and zeropoint energy of the molecule. 4+3+3
8. (a) If ψ_a and ψ_b are two atomic orbitals of a diatomic molecule that are allowed to mix to form molecular orbital, show that LCAO-MO method leads to the secular determinant :

$$\begin{vmatrix} H_{aa} - E & H_{ab} - E S_{ab} \\ H_{ab} - E S_{ab} & H_{bb} - E \end{vmatrix} = 0$$

What are the expressions for the quantum mechanical integrals, H_{aa} , H_{ab} , S_{ab} ?

- (b) State and explain 'Mutual Exclusion Principle' and hence, identify which fundamental vibrations are Raman-active or, IR-active in CO_2 molecule.
- (c) The following mechanism has been proposed for the dimerization of Anthracene in Benzene :



Using the steady state approximation for A^* , prove that quantum yield of A_2 is independent of the intensity of the light absorbed, where I_{abs} is the intensity of the radiation absorbed. 4+3+3

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9. (a) How can you determine the bond length for N_2 molecule using rotational spectroscopy?
 (b) Describe the principle of Lindemann theory for unimolecular reaction.
 (c) Determine the probability of finding a classical harmonic oscillator in the classically forbidden region for $v = 0$ (ground state).

Given, $\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\frac{\alpha x^2}{2}}$ Int. $= \int_1^{\alpha} e^{-z^2} dz = 0.1394$ 4+3+3

10. (a) Show that the two maxima of $r^2\psi_{2s}(r)$ against r occur at $(3 \pm \sqrt{5})a_0$. Find the nodal point for the radial distribution for ψ_{2s} wave function.

Given, $\psi_{2s} = \sqrt{\frac{1}{32\pi}} \left(\frac{1}{a_0}\right)^{\frac{3}{2}} \left(2 - r/a_0\right) e^{-r/2a_0}$

- (b) State Frank Condon principle. State its significance. What is Frank Condon factor?
 (c) What is the physical basis of Born-Oppenheimer approximation? 4+3+3