3 (Sem–5/CBCS) CHE HC 2

2024

CHEMISTRY

(Honours Core)

Paper : CHE–HC–5026

(Physical Chemistry – V)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

1. Answer the following as directed : 1×7=7

   (a) State whether the following statement is True ***or*** False :
   State function ψ of a system must be an eigenfunction of the operator $\hat{H}$.

   (b) Indicate whether the function $\psi = e^{-x}$ is acceptable as wave function or not. $(-\infty \leq x \leq \infty)$

(c) Show whether the operator $\hat{O}$ in the equation $\hat{O}\psi = \psi^2$ is linear or not.

(d) State the rule of mutual exclusion in connection with Raman spectroscopy.

(e) State the basic difference between line spectrum and continuous spectrum.

(f) Calculate the energy per mole of light having wavelength of 8000Å.

(g) What are photosensitizers ? Give *one* example.

2. Answer the following questions : 2×4=8

(a) Normalize the function :

$$\psi = \sin\frac{\pi x}{a}; 0 \leq x \leq a$$

(b) It is required that the eigenfunction of an operator representing a physical quantity should be single-valued, continuous and quadratically integrable. State why the function should be single-valued and continuous.

(c) What is the lowest vibrational energy in terms of oscillation frequency for a diatomic molecule undergoing simple harmonic motion ? Give the expression. What does it imply ?

(d) The Stokes' lines are more intense than the anti-Stokes' lines. Explain.

3. Answer ***any three*** questions : 5×3=15

(a) (i) A certain system is described by the operator $\hat{A} = -\frac{d^2}{dx^2} + x^2$.

Show that $\psi = \left(xe^{-x^2/2} \right.$ is eigen-function of $\hat{A}$.
What is the eigenvalue ? 2+1=3

(ii) Calculate the spacing between the first two energy levels for an electron in a one-dimensional box of 1·0Å length. 2

(b) Write how the molecular orbitals of a homonuclear diatomic molecule can be classified as σ and π. Which of these two is doubly degenerate and why ? What is the basis of classifying the *MOs* as g and u ? 2+2+1=5

(c) The first line in the pure rotational spectrum of HCl appears at $21{\cdot}18\ cm^{-1}$. Calculate the bond length of the molecule. Given atomic masses of H and Cl are $1{\cdot}008\ amu$ and $35{\cdot}45\ amu$ respectively.

$\left(1\,amu = 1.66 \times 10^{-27}\ kg\right)$ 5

(d) (i) What do you mean by fingerprint region in IR spectroscopy ? Explain with example. 1+1=2

(ii) Write the quantum mechanical theory of Raman effect. What do you mean by Raman shift ? 2+1=3

(e) The decomposition of HI takes place by the following mechanism :

$HI + h\nu \rightarrow \dot{H} + \dot{I}$

$\dot{H} + HI \rightarrow H_2 + \dot{I}$

$\dot{I} + \dot{I} \rightarrow I_2$

Find an expression for the rate of the reaction. Also find the quantum efficiency of the reaction. 3+2=5

4. Answer ***any three*** questions : 10×3=30

(a) (i) What is a Hermitian operator ? Show that the eigenvalue of a Hermitian operator is real. 2+3=5

(ii) Evalute the expectation values of $\langle \hat{x} \rangle$ and $\langle \hat{p}_x \rangle$ for the ground state of the harmonic oscillator. Given normalized wave function

$$\psi_{(x)} = \left(\sqrt{\frac{a}{\pi}}\right) e^{-ax^2/2} ;$$

standard integral

$$\int_{-\infty}^{\infty} x^2 e^{-ax^2}\, dx = \left(\frac{1}{2a}\right)\left(\frac{\pi}{a}\right)^{1/2} \qquad 5$$

(b) (i) Write the general expressions for the magnitude and z-component of angular momentum. Write what you mean by space quantisation of angular momentum. Discuss with diagram the orientations of angular momentum of magnitude $\sqrt{2}\hbar$ in presence of applied magnetic field in z-direction. 1+2+2=5

(ii) Write what do you mean by radial distribution function. Find an expression for the radial distribution function. Draw the plot of radial distribution function against the radial distance from the nucleus for 1*s* orbital. State how this plot differs from the plot of square of the radial function against the radial distance.

1+2+1+1=5

(c) (i) Discuss the LCAO-MO concept with respect to the hydrogen molecule ion. 5

(ii) Why does He_2^+ exist whereas He_2 does not ? 2

(iii) For a particle in a, one-dimensional box of length a, find the probability of finding the particle in the region $0 \leq x \leq \frac{a}{4}$ in the ground state. 3

(d) (i) Show that for a rotational spectrum of a diatomic molecule, the rotational quantum number (to the nearest integer value) for the maximum populated level is given

by $J_{max} = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}$

5

(ii) Considering diatomic molecule to be an anharmonic oscillator, deduce the energy expressions for the allowed vibrational transitions. Explain fundamental absorption and overtones. 5

(e) (i) Using the Franck-Condon principle, explain why the intensities of the vibrational lines associated with electronic transitions differ. 3

(ii) Define auxochrome. What do you mean by red shift and blue shift of absorption maximum ? 1+1=2

(iii) In the pure rotational spectra of ^{14}NO and ^{15}NO, the first lines appear at $3{\cdot}4\,cm^{-1}$ and $3{\cdot}2815\,cm^{-1}$ respectively. If the atomic massess of ^{14}N and O are 14·004 *amu* and 15·9994 *amu*, respectively, find the atomic mass of ^{15}N. 5

(f) (i) Write the mechanism of the $H_2 - Cl_2$ photochemical reaction. Prove that the rate of formation of HCl is directly proportional to the intensity of the absorbed radiation. 2+3=5

(ii) In a certain photochemical reaction using 464 *nm* radiation, the incident light power was 16·0 W and the system absorbed 75% of the incident light. The quantum yield of the reaction was found to be 0·15. How many moles of the product were formed in the reaction in 100s ? 5
