Total number of printed pages–11

3 (Sem–5/CBCS) CHE HC 2

2022

CHEMISTRY

(Honours)

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 **any seven** of the following as directed : 1×7=7

   (a) Find the eigenvalue of the operator $\dfrac{d^2}{dx^2}$ if the eigenfunction is $\cos 2x$.

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

(c) The ground state electronic configuration of H_2^+ is $(1s\sigma_g)^1$. Write the term symbol.

(d) The one-particle wave function $\psi(x, y, z, t)$ has the dimensions ———. *(Fill in the blank)*

(e) A spin-orbital can accommodate a maximum of ——— electron(s). *(Fill in the blank)*

(f) What is the energy $(in\,kJmol^{-1})$ of visible rays with $\lambda = 400\,nm$?

(g) State which of the following will be microwave active :

CH_4, CH_3Cl, SF_6, OCS

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

(i) State which of the normal vibrations of CO_2 is Raman active.

(j) Write the difference between chemical reaction and photochemical reaction in terms of Gibbs free energy change.

(k) State what is meant by quantum yield for photochemical reactions.

(l) In photosynthesis, CO_2 reacts with water in presence of chlorophyll and other plant pigments to produce starch. State the role of chlorophyll and the other pigments in the reaction.

2. Answer *any four* of the following questions :

$2\times4=8$

(a) Normalise the H-like function $\psi = e^{-n}$.

(b) Show that the wave function for a particle in one-dimensional box of length a, where the potential energy is zero, is not an eigenfunction of the linear momentum operator in one dimension.

(c) Define complementary observable with *one* example.

(d) Show that the functions $sin\dfrac{\pi x}{a}$ and $cos\dfrac{\pi x}{a}$ are orthogonal within the limit $0 \le x \le a$.

(e) Calculate the energy difference between the two rotational levels in joule of a molecule if it absorbs a photon of wavelength $10\,cm$.

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

(g) What do you mean by characteristic group frequencies in IR spectroscopy ? Explain with example.

(h) A sample of gaseous HI was irradiated by light of wavelength $253 \cdot 7\,nm$ when $307\,J$ of energy was found to decompose $1 \cdot 30 \times 10^{-3}\,mole$ of HI. Calculate the quantum yield for the dissociation of HI.

3. Answer any three questions :

(a) (i) Write down the Schrödinger equation for a particle of mass m moving in three dimensions and state the properties of wave function to have physical significance. $1+2=3$

(ii) The functions $\psi_1 = \left(\dfrac{1}{\pi}\right)^{\frac{1}{2}} \cos x$ and $\psi_2 = \left(\dfrac{1}{\pi}\right)^{\frac{1}{2}} \sin x$ are defined in the interval $x = 0$ to $x = 2\pi$. Examine if the functions are orthogonal to each other. 2

(b) (i) Write down the Schrödinger equation for the hydrogen-like system in spherical polar coordinates and separate it into radial and angular equations. 3

(ii) What do you mean by orbital ? State the differences between an orbit and an orbital. 2

(c) Write what you mean by radial distribution function. Find an expression for the radial distribution function. Give the plot of radial distribution function against the radial distance from the nucleus for 1s orbital. State how this plot differs from the plot of square of the radial function against the radial distance. $1+2+1+1=5$

(d) 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

(e) Name the main electronic transitions observed in organic molecules. Indicate the regions of wavelengths where these transitions may take place. What types of electronic transitions are observed in carbonyl chromophore ? Mention the effect of conjugation on these transitions.   3+1+1=5

(f) (i) Which of the following molecules will show infrared absorption spectra ?

HBr, N_2, H_2O, CN
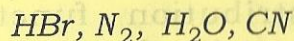
Mention the reason of infrared absorption.   2

(ii) The fundamental vibration frequency of HCl is $2,890 \ cm^{-1}$. Calculate the force constant of this molecule.   3

(g) Discuss the mechanism of the photochemical reaction between hydrogen and bromine and find the expressions for the reaction rate and the quantum yield for this reaction.

5

(h) What do you mean by the term 'quenching of fluorescence'? Derive Stern-Volmer equation.   2+3=5

4. Answer *any three* questions :

(a) (i) Using the MO wave function of H_2 discuss the drawback of the MO theory. Write how Heitler-London modified the wave function. Discuss about the correct form of the wave function for bonding in H_2 taking into account of resonance.   3+1+3=7

(ii) Show that the maximum probability of finding the electron of H-like atom in the ground state is at a distance of a_0/z from the nucleus.   3

(b) (i) Derive expression for the total energy of a particle in a three-dimensional box. Explain the concept of degeneracy. 5+2=7

(ii) For a particle in a one-dimensional box of length a, find the probability of finding the particle in the region $0 \le x \le a/4$ in the ground state. 3

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

(ii) Evaluate the expectation values of $\langle x \rangle$ and $\langle p_x \rangle$ for the ground state of the harmonic oscillator. Given normalized wave function

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

standard integral

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

(d) (i) A particle in a box cannot have zero energy quantum mechanically. Explain. 3

(ii) Find the values of momentum and energy for an electron in a box of length $1A°$ for $n = 1, 2$. 4

(iii) Prove that $\psi(x) = e^{iCx}$ is acceptable eigenfunction where C is finite constant. 3

(e) (i) Using the anharmonic oscillator concept, deduce expressions for the energy required for allowed vibrational transitions. Indicate fundamental absorption and overtones. 5

(ii) Write how will you distinguish between ethanol and ethanol by using IR spectra. 2

(iii) The fundamental vibrational frequency of $H^{35}Cl$ is $8 \cdot 667 \times 10^{31} s^{-1}$. What would be the separation between the infrared absorption lines for $H^{35}Cl$ and $H^{37}Cl$, if the force constants of the bonds are assumed to be same? 3

(f) (i) Write the quantum mechanical theory of Raman effect. What do you mean by Raman shift? Explain the conditions under which Stokes and anti-Stokes lines are observed. 2+1+2=5

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

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

(g) (i) What is called photostationary state of the photochemical reaction? The following mechanism has been proposed for the dimerization of anthracene:

(i) $A + h\nu \xrightarrow{k_1} A^*$

(ii) $A^* + A \xrightarrow{k_2} A_2$

(iii) $A^* \xrightarrow{k_3} A + h\nu'$
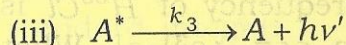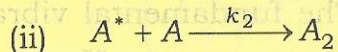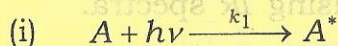
Show that when the reaction is at photostationary state and presence of large amount of monomer, the concentration of dimer is independent of the concentration of monomer. 1+4=5

(ii) Write a note on chemiluminescence. 2

(iii) For the photochemical reaction

$A \rightarrow B$;

1×10^{-5} moles of B were formed on absorption of $6 \cdot 62 \times 10^7$ ergs at $3600 A°$. Calculate the quantum yield of the reaction. 3

(h) (i) Define transition moment. What do you mean by allowed and forbidden transitions in the context of transition moment? 3

(ii) The lifetime of an excited electronic state is 10^{-8}_s. Calculate the width of the spectral line in Hz. 2

(iii) State and explain the factors on which the width of a spectral line depends. 3

(iv) Write the selection rules of molecular electronic transition in diatomic molecules. 2

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