Total No. of Printed Pages—7

5 SEM TDC CHMH (CBCS) C 12

2022

(Nov/Dec)

CHEMISTRY

(Core)

Paper : C–12

(Physical Chemistry, Quantum Chemistry and Spectroscopy)

Full Marks : 53
Pass Marks : 21

Time : 3 hours

The figures in the margin indicate full marks for the questions

2022 5th SEM CHEMISTRY

1. Choose the correct answer from the following : 1×4=4

(a) The expression for Hamiltonian operator $\hat{H}$ is

(i) $\frac{h^2}{8\pi^2 m}\nabla^2 + V$

(ii) $-\frac{h^2}{8\pi^2 m} + V$

(iii) $\frac{h^2}{8\pi^2 m}\nabla^2 - V$

(iv) $-\frac{h^2}{8\pi^2 m}\nabla^2 - V$

(b) The eigenvalue of the function $\psi = 8e^{4x}$ is

(i) e^{4x}

(ii) 32

(iii) 8

(iv) 4

(c) The rotational spectrum of a rigid diatomic rotator consists of equally spaced lines with spacing equal to

(i) B

(ii) $2B$

(iii) $B/2$

(iv) $4B$

(d) Intersystem crossing refers to

(i) transition between two states of a system

(ii) radiationless transition between states of different spin multiplicities

(iii) transition between excited and ground states with same multiplicity

(iv) All of the above

(Continued)

2. Answer any *four* questions from the following : 2×4=8

(a) HBr molecule is microwave active. Explain, why.

(b) Describe Larmor frequency.

(c) Water is a good solvent for UV and visible spectroscopy, but not for IR spectroscopy. Explain.

(d) Distinguish photochemical reaction from thermal reaction.

(e) State whether the function

$$\psi = \sin(k_1 x)\sin(k_2 y)\sin(k_3 z)$$

is an eigenfunction of the operator ∇^2. If it is an eigenfunction, find eigenvalue.

UNIT—I

3. Answer any *four* questions from the following : 4×4=16

(a) Solve Schrödinger's wave equation for a particle having mass m moving freely in a one-dimensional box of length a. Find out the energy expression. 3+1=4

(Turn Over)

(b) What is a simple harmonic oscillator? Deduce an expression for the fundamental frequency of a harmonic oscillator. 1+3=4

(c) (i) What is an operator? Write quantum mechanical operator corresponding to momentum. 1+1=2

(ii) Examine if the function

$\psi_1(x) = N_1(a^2 - x^2)$ and $\psi_2(x) = N_2 x(a^2 - x^2)$

are orthogonal within $-a < x < a$. 2

(d) (i) Show that Hamiltonian operator ($\hat{H}$) for a rigid rotator is given by $\hat{H} = L^2/2I$, where L is the angular momentum and I is the moment of inertia. 2

(ii) Write the energy expression for second energy-level of a rigid rotator. 2

(e) (i) Write Schrödinger wave equation for hydrogen atom in Cartesian and polar coordinate. 1+1=2

(ii) What does the term 'degenerate level' mean? Calculate degeneracy of the level having energy $\frac{5h^2}{8ma^2}$ for a free particle moving in a two-dimensional box of two equal side lengths. 1+1=2

(Continued)

(f) (i) What is zero point energy? Calculate zero point energy of a molecule if it is considered as a simple harmonic oscillator. 2

(ii) Sketch and explain the wave functions for the first three energy levels for the particle in one-dimensional box. 2

UNIT—II

4. Answer any *four* questions from the following : 4×4=16

(a) Describe different types of electronic transitions with one example of each.

(b) State Frank-Condon principle. Explain the effects of change of solvents on $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. Write the significance of molar extinction coefficient. 1+2+1=4

(c) The C—H vibration (stretching) in chloroform occurs at 3000 cm^{-1}. Calculate the C—D frequency (stretching) in deutero chloroform. It is supposed force constants remain same during isotopic substitution.

(Turn Over)

(d) Write brief notes on the following : $2\times2=4$

(i) Chemical shift

(ii) Spin-spin coupling

(e) (i) Discuss the effect of isotopic substitution on the rotational spectra of a diatomic molecule. 2

(ii) Roughly sketch the fundamental vibrations of water molecule and show the infrared active vibrations. 2

UNIT—III

5. Answer any *two* questions from the following : $4\frac{1}{2}\times2=9$

(a) What is quantum yield of a photochemical reaction? Under what condition is its value 1? A certain system absorbs 3×10^{20} quanta of light per second. On irradiation for 20 minutes, 0·02 mole of the reactant was found to have reacted. Calculate the quantum yield of the reaction.

(b) What are photochemical reactions? Write the differences between photochemical and thermal reactions. Discuss the reasons for high and low quantum yields of photochemical reactions. $1+1+2\frac{1}{2}=4\frac{1}{2}$

(Continued)

(c) (i) Write a short note on any *one* of the following : 2

(1) Actinometry

(2) Chemiluminescence

(ii) Write the differences between phosphorescence and fluorescence. $2\frac{1}{2}$

★★★