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5 SEM TDC CHMH (CBCS) C 12

2021

(Held in January/February, 2022)

CHEMISTRY

(Core)

Paper : C–12

(Physical Chemistry)

Full Marks : 53

Pass Marks : 21

Time : 3 hours

The figures in the margin indicate full marks for the questions

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

   (a) The degeneracy of rotational level of a diatomic molecule having energy $\frac{h^2}{4\pi^2 I}$ is

      (i) 0

      (ii) 1

      (iii) 2

      (iv) 3

(Turn Over)

(b) Vibrational transition exists in

(i) infrared region

(ii) microwave region

(iii) visible region

(iv) radio-frequency region

(c) The degeneracy of a particle of mass m confined in a three-dimensional box having energy level equal to $\frac{14h^2}{8ma^2}$ is

(i) 7

(ii) 14

(iii) 6

(iv) 8

(d) In photosynthesis, chlorophyll acts as a

(i) catalyst

(ii) photosensitizer

(iii) photoinhibitor

(iv) All of the above

2. Answer any *four* questions from the following : $2 \times 4 = 8$

(a) Microwave studies are done only in gaseous state. Explain.

(b) Explain why the nuclei H^1 and ^{13}C are suitable for NMR investigation.

(c) Write a short note on fingerprint region.

(d) What is chemiluminescence? Give one example.

(e) Show that the functions $\psi_1 = \left(\frac{1}{2\pi}\right)^{1/2}$ and $\psi_2 = \left(\frac{1}{\pi}\right)^{1/2} \cos x$ in the interval $x = 0$ to $x = 2\pi$ are orthogonal to each other.

(f) Show that $\sin 4x$ is an eigenfunction of the operator $\frac{d^2}{dx^2}$. Find the eigenvalue.

UNIT—I

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

(a) What are normalized and orthogonal wave functions? For the function $\psi(\theta) = \sin\theta$, where the variable θ changes continuously from 0 to 2π, determine whether it is normalized or not. If it is not, find the normalization factor. 1+2+1=4

(Turn Over)

(b) ψ_i and ψ_j represent the wave function corresponding to two different states of a particle moving freely in a one-dimensional box. Show that they are orthogonal to each other. 4

(c) Consider a particle of mass m confined in a two-dimensional box of edge lengths a and b. Find the energy and wave functions by solving the Schrödinger's equation. The potential energy

$$V(x, y) = 0, \quad \text{for } 0 \le x \le a \text{ and } 0 \le y \le b$$
$$= \infty, \quad \text{elsewhere}$$

Also write the expression for energy when $a = b$. 3+1=4

(d) *(i)* What does the term 'degenerate levels' mean? Determine the degree of degeneracy of the level $\frac{17h^2}{8ma^2}$ of a particle in a cubical box. 1+1=2

(ii) Form Schrödinger wave equation for a one-dimensional simple harmonic oscillator. 2

(e) (i) The distance between the atoms of a diatomic molecule is r and its reduced mass is μ. If the angular momentum is L and moment of inertia is I, then prove that kinetic energy $T = \dfrac{L^2}{2\mu r^2}$. 3

(ii) Write the expression for energy for a rigid rotator. 1

(f) (i) Write down the Schrödinger wave equation in polar form for H-atom. 1½

(ii) Calculate the most probable distance r_{mp} of the electron from the nucleus in the ground state of hydrogen atom, given that the normalized ground state wave function is

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

Given $a_0 = 0{\cdot}529$ Å. 2½

(g) (i) Write down the equation showing Hamiltonian operator for one-dimensional harmonic oscillator. 2

(Turn Over)

(ii) Sketch the variation of radial probability density against the distance from the nucleus for 2s state for hydrogen atom. 2

UNIT—II

4. Answer any *two* questions from the following : 8×2=16

(a) *(i)* Show that the lines in the rotational spectrum of a diatomic molecule are equispaced under the rigid rotator approximation. 3

(ii) A transition from $J = 0$ to $J = 1$ in the rotational spectrum of CO corresponds to $3{\cdot}84235\ \text{cm}^{-1}$. Calculate the moment of inertia and bond length. 2+2=4

(iii) Write the selection rule for rotational spectra. 1

(b) *(i)* Show that the frequency of the absorbed radiation in pure vibrational spectra is equal to the fundamental frequency of vibration ν_0 of the molecule. 2½

(ii) Prove that the ratio of wave numbers of fundamental, first overtone and second overtone is approximately 1 : 2 : 3. 2½

(iii) Roughly sketch the fundamental modes of vibrations of CO_2 and show the infrared active vibrations. 3

(c) (i) State and explain Franck-Condon principle. 3

(ii) Explain why TMS is used as a reference substance in NMR spectroscopy. 2

(iii) Calculate the NMR frequency (in MHz) of the proton (^1H) in a magnetic field of intensity 1·4092 tesla, given that $g_N = 5{\cdot}585$ and $\mu_N = 5{\cdot}05 \times 10^{-27}$ JT^{-1}. 2

Or

Briefly discuss Born-Oppenheimer approximation.

(iv) Write any one difference between fluorescence and phosphorescence. 1

(Turn Over)

UNIT—III

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

(a) State and explain Lambert-Beer law. Write the significance of molar extinction coefficient. $4\frac{1}{2}$

(b) Explain the term 'quantum yield'. Discuss briefly the reasons for high and low quantum yields. $1\frac{1}{2}+3=4\frac{1}{2}$

(c) What is photochemical equilibrium? Give example of a photochemical equilibrium in which only one reaction is light sensitive. Deduce an expression for equilibrium constant of a photochemical equilibrium. $1+1+2\frac{1}{2}=4\frac{1}{2}$

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