December 2022

B.Sc. (H) Chemistry - V SEMESTER

Physical Chemistiy - V (BCH-502)

Time : 3 Hours] [Max. Marks : 75

Instructions.:

1. *It is compulsory to answer all the questions (1.5 marks each) of Part-A in short.*
2. *Answer any four questions from Part-B in detail.*
3. *Different sub-parts of a question are to be attempted adjacent to each other.*
4. *All the symbols represent usual meaning related to physical chemistry.*

PART-A

1. (a) The work function of Cesium metal is 2.14 eV. Calculate the speed of emitted e^- when metal is exposed to light with 700 nm wavelength.

[CO:1, PO:2-5]

(1.5)

(b) For an electron in a 12 eV deep one-dimensional well width of 3 Å, calculate the number of bound states?

[CO:1, PO:2-5]

(1.5)

(c) Calculate the energy required for a transition from $n_x = n_y = n_z = 1$ to 2nd degenerate energy level for an electron in a cubic hole of a crystal having edge length of 1 Å. [CO:1-3, PO:2-5]

(1.5)

(d) Calculate the force constant of HCl bond if fundamental vibrational frequency is 8.667×10^{13} sec^{-1}.

[CO:4, PO:2-5]

(1.5)

(e) For a particle in the stationary state n of 1-D box of length a, find the probability for the particle in the region $0 \geq x \geq a/4$. Calculate for n = 1 & 2.

[CO:1-3, PO:2-5]

(1.5)

(f) If 10 distinguishable particles are distributed as each successive energy levels have one less particle than previous with an increase in energy, where the first and second exited states are triply degenerate. Calculate maximum probable microstates of the system?

[CO:1-4, PO:2-5]

(1.5)

(g) Assume that a particle of mass 'm' is confined to a cubic box and its energy is $101\ h^2/8\ ma^2$. What is the degeneracy of this level?

[CO:1-4, PO:2-5]

(1.5)

(h) If $\check{Z}$ and $\hat{Y}$ are two operators such that $[\check{Z}, \hat{Y}] = 8$, then find out value for $[\check{Z}, \hat{Y}^2]$? [CO:1, PO:2-5]

(1.5)

(i) Which of the statement is **false**' regarding Bohr's theory,

(i) It introduces idea of stationary states.

(ii) It explains line spectrum.

(iii) It gives probability of electron near nucleus.

(iv) It predicts angular momentum of electron.

[CO:1-2, PO:2-5]

(1.5)

(j) (**A**) A molecule to give pure rotational Raman spectrum, the polarizability of the molecule must be an isotropic (**R**) Polarizability depends on orientation of the molecule w.r.t. direction of electric field.

(i) **A** and **R** both correct.

(ii) Only **A** is correct.

(iii) **A** and **R** both correct but **R** is not correct explanation of **A**. [CO:4, PO:2-5]

(1.5)

PART-B

2. (a) A particle in an infinite square well, $V(x) = 0$ for $0 < x < L$, $V(x) = 1$ otherwise. Verify that $\psi = A \sin kx$ and $\psi = A \exp(ikx)$ are eigenfunction of the Hamiltonian operator for the particle. What is the eigenvalue and energy at **zero** temperature? Draw wave function and probability density for energy level n = **2** and n = **4**. [C0:1, PO:2-5]

(10)

(b) Explain Plank's radiation Law. How does it explain classical concept of distribution of black body radiation? [C0:1, PO:2-5]

(5)

3. (a) If a particle is in two-dimensional box with side **a** and **b**,

(i) Calculate energy for **n** = 1, 2 and 4 given that **2b** = **a**.

(i) Comment on first three degenerate states and zero-point energy for above two-dimensional box.

[CO: 1-3, PO:2-5]

(10)

(b) How many vibrational modes exist in H_2O and CCl_4? Show calculations. [CO:4, PO:2-5]

(5)

4. (a) Define spin-multiplicity. Sketch radiative and non-radiative process of photochemistry.

[CO:2-3, PO:2-5]

(10)

(b) Find out all possible degenerate states for particle in two-dimensional box up to **n** = **5**. [CO:1-4, PO:2-5]

(5)

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5. (a) Derive relationship for Maxwell-Boltzmann statistics for distribution of particles over energy states in thermal equilibrium. [CO:4, PO:2-5]
(10)

(b) Find out entropy of a system having uniform distribution of **10** distinguishable particles in **five** energy levels, where the second and fourth exited states are doubly and triply degenerate respectively. [CO:4, PO:2-5]
(5)

6. (a) Sketch vibrational-rotational spectral energy diagram and explain **P, Q** and **R** branches in detail.
[CO:3-4, PO:2-5]
(10)

(b) Describe Hermitian Operator and its characteristics in quantum mechanics. Prove that average value of the square of Hermitian operator is always positive.
[CO:1-2, PO:2-5]
(5)

7. (a) Draw first, second and fourth vibrational wave functions. Comment on symmetry of first three vibrational energy levels of harmonic oscillator and their impact on oscillations? [CO:4, PO:2-5]
(5)

(b) The infra-red spectrum of $^{75}Br^{19}F$ consist of an intense line at 380 cm^{-1}. Calculate the force constant of $^{75}Br^{19}F$? [CO:4, PO:2-5]
(5)

(c) What are the consequences of continuous increase in length of box for particle in 1-D box. What happen if the infinite potential barrier walls of the 1-D box are suddenly removed? [CO:1, PO:2-5]

(5)