TDC (CBCS) Odd Semester Exam., 2020
held in March, 2021

CHEMISTRY

(5th Semester)

Course No. : CHMHCC-502T

(Physical Chemistry—V)

Full Marks : 50
Pass Marks : 20

Time : 3 hours

The figures in the margin indicate full marks for the questions

SECTION—A

1. Answer any *ten* of the following questions : 2×10=20

(a) Write four important postulates of quantum mechanics.

(b) What do you mean by the term 'zero point energy'?

(c) A hockey ball of mass 0·2 kg moving with a velocity of 3×10^{3} ms^{-1}. If the ball can be located within an error equal to 600 nm, calculate the uncertainty in momentum of the ball as compared with the momentum of the ball itself.

(d) Determine the degree of degeneracy of the energy level $\frac{17h^2}{8ma^2}$ of a particle of mass m in a 3D cubical box of length a.

(e) Mention the important features of LCAO method for construction of molecular orbitals.

(f) Mention two similarities and dissimilarities between valence bond method and molecular orbital method.

(g) State and explain variation theorem.

(h) Draw the molecular orbital diagram for HF molecule.

(i) Explain Born-Oppenheimer approximation.

(j) What is the moment of inertia of a diatomic molecule whose inter-nuclear distance is 150 pm and the reduced mass is $1{\cdot}5\times10^{-27}$ kg?

(k) Mention selection rules for vibrational transitions in a simple harmonic oscillator.

(l) Explain the concept of group frequencies in vibrational spectroscopy.

(m) Elucidate the rule of mutual exclusion.

(n) What do you mean by Stokes and anti-Stokes lines?

(o) Mention the differences between fluorescence and phosphorescence.

(p) Explain the term 'chemical shift'.

(q) What do you understand by photosensitized reaction? Give an example.

(r) Write the different characteristics of electromagnetic radiation.

(s) Explain the term 'quenching' with an appropriate example.

(t) What do you understand by actinometry?

SECTION—B

Answer *any* **five** questions

2. State Heisenberg uncertainty principle. Verify the Heisenberg principle for the ground state of 1-D simple harmonic oscillator. 1+5

3. (a) Solve the Schrödinger's wave equation for a particle of mass m confined in a 1-D box of length a and moving along x-axis. 4

(b) "The vibrational energy levels of a diatomic simple harmonic oscillator are equidistant." Explain with the help of a diagram. 2

4. *(a)* Write the Schrödinger wave equation for H-atom in *(i)* Cartesian coordinates (x, y, z) and *(ii)* spherical polar coordinates (r, θ, ϕ) and separate it into three equations. 1+3

(b) Calculate the most probable distance (r_{mp}) of the electron from the nucleus. 2

5. Apply LCAO-MO theory to H_2^+ ion to derive the secular determinant. Solve it to find the energy levels and the corresponding normalized wave functions. 3+1½+1½

6. Derive an expression for the relational energy of a diatomic molecule, if it is a rigid rotator. Draw the energy level diagram. Also show that the energy difference between the adjacent lines in the rotational spectrum of a diatomic molecule is constant. 3+1+2

7. *(a)* With respect to vibration-rotation spectroscopy, explain the formation of *P*, *Q* and *R* branches. 3

(b) The fundamental vibrational frequency of HCl is 2890 cm^{-1}. Calculate the force constant of the molecule. 3

8. *(a)* What are the requirements for a vibration to be *(i)* IR active and *(ii)* Raman active? 3

(b) Explain the terms *(i)* singlet and *(ii)* triplet with respect to electronic spectroscopy, taking suitable example. 3

9. *(a)* Discuss in detail the principle of nuclear magnetic resonance spectroscopy. 3

(b) Taking two suitable examples of organic molecules, explain their PMR spectra. 3

10. *(a)* State and explain the first law of photochemistry. 2

(b) Define quantum yield. What should be the quantum yield for primary processes in photochemical reaction? 2

(c) Explain the significance of absorption coefficients. 2

11. *(a)* State and explain second law of photochemistry. 2

(b) Mention two limitations of Lambert-Beer law. 1

(c) On passing monochromatic light through a 0·4 *M* solution of a substance in a cell 2 cm thick, the intensity of the transmitted light was reduced to 50%. Calculate the molar extinction coefficient of the substance. 3

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