2009

M.Sc.

2nd Semester Examination

CHEMISTRY (PHYSICAL)

PAPER—CH-1201

Full Marks : 40

Time : 2 Hours

The questions are of equal value.

The figures in the right-hand margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

Group—A

Answer any *two* of the following.

1. (a) Using the ladder operator technique find out the energies and wave functions in normalised form of harmonic oscillator. 5+5

2. (a) Show that $\langle \psi_{nlm} | \psi_{n'l'm'} \rangle = \delta_{nn'}\delta_{ll'}\delta_{mm'}$. 6

(b) Explain normal Zeeman effect. 4

3. (a) Show that the orbitals of H-atom have n^2 fold degeneracy. 4

(b) Derive the operator form of $\hat{L}^2$ in spherical polar co-ordinate system. 6

4. (a) Find the commutator of $\overline{H}$ and $a_{\pm}^{n}$ for a linear harmonic oscillator. The symbols have their usual meaning. 6

(b) Find out $[L^2, Z]$. 4

Group—B

Answer any *one* of the followings.

5. (a) Define Oscillating reaction with a suitable example. 4

(b) What are complementary and non-complementary electron transfer reactions? Give example. 3

(c) The protein catalase catalyzes the reaction

$$2H_2O_2\,(aq) \longrightarrow 2H_2O\,(l) + O_2\,(g)$$

and has a Michaelis constant of $K_m = 25 \times 10^{-3}$ mol dm^{-3} and a turnover number of 4.0×10^7 S^{-1}. Calculate the initial rate of this reaction if the total enzyme concentration is 0.016×10^{-6} mol dm^{-3} and the initial substrate concentration is 4.32×10^{-6} mol dm^{-3}. Calculate v_{max} for this enzyme. Catalase has a single active site. 3

6. (a) What do you mean by asymmetry and electrophoretic effects? Compute electrophoretic component of velocity of a moving ion. 2+2+2

(b) Write short note on dispersion of conductance. 4

7. (a) When does the concentration overpotential arise? Derive an equation relating concentration overpotential and limiting current density. 2+5

(b) How do you obtain equilibrium exchange current density using high field aproximation of Butler Volmer equation? 3

Group—C

Answer any *one* of the followings.

8. (a) Lennard-Jones 6–12 potential is given by the following expression :

$$V = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

where 'ϵ' is the depth of the potential well, 'σ' is the internuclear separation at $V = 0$.

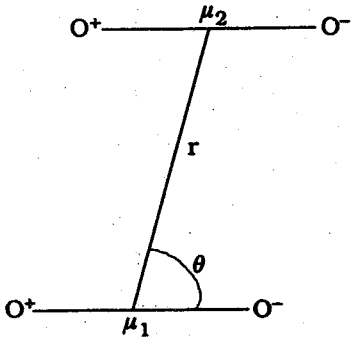
Give a Schematic plot of the potential w.r.t. internuclear distance. Obtain an expression for 'r' where potential has minimum value. 4

(b) Draw a Schematic potential energy diagram for the ground and the first excited singlet state for Salicylic acid w.r.t. its intramolecular proton transfer co-ordinate. 2

(c) (i) Non-centrosymmetric crystals i.e. where g–u mixing occurs in the molecular wavefunctions are used for second harmonic generation. — Explain. 2

(ii) For centrosymmetric molecule g–u transition is forbidden one in magnetic dipole mechanism. — Justify or criticize the statement. 2

9. (a) Show that the potential energy of dipole-dipole interaction (V_{d-d}), for two dipoles arranged in the following orientation,



is given by,

$$V_{d-d} = \frac{\mu_1\mu_2}{4\pi\epsilon_0 r^3}\left(1 - 3\cos^2\theta\right).$$ 7

(b) Write a short note on London dispersion force. 3

10. (a) Define hydrogen bonding and state why water is the most perfectly hydrogen bounded liquid compared to liquid NH_3 or HF. 4

(b) Derive the Debye-Langevin equation and discuss its use in determining the molecular properties. 6