GDE-1767 Seat No._____

M. Sc. (Sem. I) Examination

January – 2016

CHN-403(P) : Physical Chemistry Paper - III

Time : 3 Hours] [Total Marks : 70

Instructions : (1) Attempt all questions.
(2) All questions carry equal marks.

1 (a) Write any 02 of the following. 2×5=10

(1) Derive an equation for total energy for a particle in one dimensional box.

(2) Define operator, rules for setting up quantum mechanical operator and derive momentum operator.

(3) Prove that for any trial function Ψ, the expected value of energy $(\bar{E})$ is greater than true value (E_0), which is the lowest energy eigen value of the Hamiltonian of the system in variation method.

(4) Derive perturbation equations to calculate correction terms for eigen values and eigen functions for the unperturbed system.

(b) Attempt any one of the following. 1×4=4

(1) Draw the list of first four eigen functions along with eigen values for a particle in a one-dimensional box whose length L and origin($x = 0$) of the coordinates system is in the middle.

(2) Write a note on variation theorem.

2 (a) Answer any two of the following. **2×5=10**

(1) Determine all the values of m_j and assign them to the various value of j for a p-electron.

(2) Discuss classical and quantum mechanical concept of angular momentum.

(3) Write a note on Huckel theory of conjugated systems.

(4) Discuss Pauli's exclusion principle and Antisymmetry in quantum mechanics.

(b) Attempt any one of the following. **1×4=4**

(1) L_x, L_y and L_z can be specified simultaneously considering them as commutators.

(2) Find the nature of eigen values and eigen functions by the effect of ladder up operator.

3 (a) Do any two the following. **2×5=10**

(1) Define partial molar properties and determine the partial molar properties of a binary mixture using apparent molar concept.

(2) Derive a relation of showing effect of ionic strength on activity coefficient using Debye Huckel's limiting law for concentrated solutions.

(3) Explain third law of thermodynamics as law of unattainability and determine the total entropy of liquids.

(4) Define phase rule and descuss its application to three component system.

(b) Attempt any one of the followings. **1×4=4**

(1) For a rection

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$

The values of absolute entropies of H_2, Cl_2 and HCl are 130.60, 222.80 and 188.00 JK^{-1} respectively, and bond energies of H-H, Cl-Cl, H-Cl are 430, 240 and 400 KJ respectively. Calculate the change in entropy, heat content and free energy for above reaction at 298K.

(2) Write a note on partial molar enthalpy.

4 (a) Answer any two of the followings. **2×5=10**

(1) Define partition function and explain thermodynamic probability.

(2) Derive equation for Electronic partition function.

(3) Prove that for any chemical reaction in biological system

$$d_i S/dt = \sum J_K X_K$$

where J_k is generalised fluxes and X_k is generalised forces.

(4) Define phenomenological laws. Derive an equation considering gradient of temperature and gradient of chemical potential as force for phenomenological laws.

(b) Do any one of the followings. **1×4=4**

(1) Derive an equation for internal energy in terms partition function.

(2) Calculate the translation energy of $H_2(1,1,2)$ for an oxygen molecule in a container of side a = 0.1 m. Express the results in S. I. units.

5 Attempt any 07 from the following. 2×7=14

(1) Laplacian operator

(2) R-S coupling

(3) Generalised angular momentum

(4) Grand canonical ensamble

(5) Irreversible thermodynamics

(6) Second law of thermodynamics

(7) Phase point

(8) Significance of Fugacity

(9) Define a harmonic oscillator

(10) Degree of freedom in phase rule.
