



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.  $2 \times 5 = 10$

- (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  $\psi$ , 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.

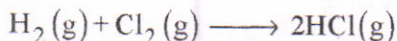
(b) Attempt any one of the following.  $1 \times 4 = 4$

- (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.  $2 \times 5 = 10$
- (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.  $1 \times 4 = 4$
- (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.  $2 \times 5 = 10$
- (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 discuss its application to three component system.

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

(1) For a reaction



The values of absolute entropies of  $\text{H}_2$ ,  $\text{Cl}_2$  and  $\text{HCl}$  are 130.60, 222.80 and 188.00  $\text{JK}^{-1}$  respectively, and bond energies of  $\text{H-H}$ ,  $\text{Cl-Cl}$ ,  $\text{H-Cl}$  are 430, 240 and 400  $\text{KJ}$  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  $\text{H}_2(1,1,2)$  for an oxygen molecule in a container of side  $a = 0.1 \text{ m}$ . 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 ensemble
  - (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.
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