



GCB-3867

Seat No. _____

M. Sc. (Sem. I) Examination

November / December - 2013

CHN - 403 : Chemistry : Paper - III

(Physical Chemistry)

(CC) (New Course)

Time : 3 Hours]

[Total Marks : 70

Instructions : (1) Write answers of all the questions in the same answer book.

(2) Each question carries 14 marks.

1 (a) Answer any two of the following : 10

(i) Set up and solve the Schrodinger wave equation for one-dimensional simple harmonic oscillator.

(ii) Explain wave function (Ψ) and its physical meaning and conditions for acceptable wave function.

(iii) Discuss the application of perturbation theory to helium atom.

(b) Answer any one of the following : 4

(i) Show that the first order stark effect on the ground state of hydrogen atom is zero.

(ii) Using the normalized trial wave function

$$\Psi = \left(\sqrt{30/a^{5/2}}\right) \times (a-x) \text{ for a particle of}$$

mass m moving inside an infinite one-dimensional box of width a , calculate the upper bound to the ground state energy and compare with the true value $h^2/8ma^2$.

- 2 (a) Answer any two of the following : 10
- Write a note on commutation relations.
 - Discuss spin angular momentum.
 - Apply the Huckel molecular orbital theory to 1,3-Butadiene.
- (b) Answer any one of the following : 4
- Using the Huckel rule, determine which of the following molecules are aromatic or non-aromatic ?
 - Benzene
 - Cyclopropenyl cation
 - Cyclopropenyl radical
 - Cyclopropenyl anion.
 - Find the terms that can arise from the configuration.
 - d^2
 - p^3
- 3 (a) Answer any two of the following : 10
- Give the concept of chemical potential and derive relation between chemical potential and partial molar entropy.
 - Write a note on excess functions for non-ideal solutions. Derive various thermodynamic functions.
 - What do you understand by term fugacity? Explain clearly that the fugacity of a gas can be less than as well as more than the pressure.

- (b) Answer any one of the following : 4
- (i) Calculate the activity coefficient of acetone and water in a solution containing 2.5 mole per cent acetone at 100 atm. pressure and 84.2°C. At this temperature, the vapour pressure of pure acetone and water are 1820 and 420 mm Hg respectively. The mole fraction of acetone in vapour is 0.470. Assume that the vapour behaves ideally.
- (ii) The differential heat contents of solutions of NaOH and H₂O in 10 ml solution at 298 K and 1 atm are -29.92 kJmol⁻¹ and -1.63 kJmol⁻¹, respectively. If the partial molar heat content of solution NaOH in an infinitely dilution of NaOH is -42.89 kJmol⁻¹, calculate the relative partial molar heat contents of NaOH and H₂O.
- 4 (a) Answer any two of the following : 10
- (i) Derive equation for canonical distribution.
- (ii) Express the third law of thermodynamics in terms of partition function.
- (iii) Derive equation for prigogines principle of minimum entropy production.
- (b) Answer any one of the following : 4
- (i) Calculate the total standard entropy of nitrogen gas at 25°C. Given that : Vibrational frequency = 2360 cm⁻¹. Moment of inertia = 13.g×10⁻⁴⁰ gm. cm⁻².
- (ii) Write a short note on "Irreversible thermodynamics and biological systems."

5 Answer any seven of the following : 14

- (i) What do you understand by "Well Behaved Functions" in quantum mechanics ?
- (ii) Explain the term variation theorem.
- (iii) Give applications of Extended Huckel Theory.
- (iv) What are the limitations of the first law of thermodynamics ? Justify the need for the second law.
- (v) Explain Randall-White method to determine activity and activity coefficient.
- (vi) Give limitations of phase rule.
- (vii) Define statistical weight factor.
- (viii) Calculate the angular momentum of a rigid diatomic rotating molecule (say, HCl) in the second rotational energy level. Compare it with the angular momentum of an electron in the 2p atomic orbital.
- (ix) Define electron density with example.
- (x) Calculate the translational partition function of a molecule of oxygen gas at 1 atm and 298 K moving in a vessel of volume 24.4 dm^3 .
($h=6.62 \times 10^{-34} \text{ JS}$, $m = 5.313 \times 10^{-26} \text{ kg}$ for O_2 ,
 $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$)