2019

Time : As in Programme

Full Marks : 50

*Answer **all** questions. The figures in the right-hand margin indicate marks.*

1. (*a*) Discuss the probability density and radial distribution function for 1*s* state of hydrogen atom. The wavefunction of hydrogen 1*s* state is 6

$$\Psi_{1s} = \frac{1}{\left(\pi a_0^3\right)^{\frac{1}{2}}} \; e^{-\pi / a_0}$$

(*b*) Derive ground state energy of helium atom by first order perturbatian theory. 6

(*c*) Prove $[L^2, L_x] = [L^2, L_y] = 0$ 5

OR

(*a*) Set up secular determinant for cyclobutadiene. Calculate roots, coefficients, E_π, delocalisation energy, electron density, charge density and bond order. 12

(*b*) A particle of mass m is confined in a one-dimensional box of length a. Calculate the probability of finding the particle in the following region : 5

$0 \leq x \leq a/2$

2. (*a*) What is partial molar volume ? How is it determined from apparent molar volume ? 2+5

(*b*) Prove for a binary system ΔG_{min} is minimum when $X_1 = X_2 = \frac{1}{2}$ 5

(*c*) What are phenomenological equations ? 5

OR

(*a*) Prove $\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$ 6

(*b*) Calculate the free energy of mixing when 10 moles of He are mixed with 20 moles Ne at 25°C. 4

(*c*) Discuss how chemical potential of a substance varies with temperature and pressure. 3

(*d*) Discuss Pauli principle by antisymmetric wave function. 4

3. (*a*) Derive expression for rotational partition function for linear diatomic molecule as 6

$$Q_r = \frac{8\pi^2 IkT}{\sigma h^2}$$

(*b*) Prove $S = K \ln\left(\frac{Q^N}{M!}\right) + RT\left(\frac{\partial \ln Q}{\partial T}\right)_V$ 8

(*c*) Calculate the number of ways of distributing distinguishable molecules *a*, *b*, *c* between three energy levels so as to obtain the following occupation number : 2

$N_0 = 1,\ N_1 = 1,\ N_2 = 1$

OR

(*a*) Establish a relationship between partition function and equilibrium constant. 5

(*b*) Prove

$$\eta_i = \frac{g_i}{e^{\alpha+\beta\epsilon_i} - 1}$$

the symbols have their usual meanings. 8

(*c*) Calculate number of ways to distribute two distinguishable objects in three boxes. 3