PG Odd Semester (CBCS) Exam., December—2016

CHEMISTRY

(3rd Semester)

Course No. : CHMCC–303

(Physical Chemistry—III)

Full Marks : 70
Pass Marks : 28

Time : 3 hours

The figures in the margin indicate full marks for the questions

Answer **five** questions, taking **one** from each Unit

UNIT—I

1. *(a)* "The entropy of a system in a definite state can be related to the probability of that state of the system." Elaborate the significance of the above statement and show how these two thermodynamic quantities can be related. 2+10=12

(b) Calculate the number of ways of arranging four distinguishable objects into two groups considering three objects and one object. Verify your result with an explicit enumeration. 2

2. *(a)* What is thermal de Broglie wavelength? 3

(b) Obtain an expression for translational partition function of one mole of gas having N indistinguishable molecules by using the concept of classical energy with stating the concept of phase space. 7

(c) Calculate the molar entropy of argon gas (M 39·948 g mol ^{1}) at 298·15K and 1 bar of pressure (1 bar = 10^{5} Pa, 1 Pa = 1 N m ^{2}).

[Given R 8·314 J mol ^{1} K ^{1}

k_B 1·380×10 ^{23} JK ^{1}] 4

UNIT—II

3. *(a)* What is vibrational temperature? 1

(b) Obtain an expression for vibrational partition function in 1D classical oscillator where energy is not quantized. 5

(c) The electronic partition function is usually just equal to the degeneracy of the electronic ground state. Justify the statement. 3

(d) By using the vibrational partition function, obtain an expression of heat capacity. Show that—

(i) as T , C_v R

(ii) as T 0, C_v 0 1+2+2=5

4. *(a)* Derive an expression for equilibrium constant of ideal gas phase reaction in terms of partition function. 7

(b) Discuss the assumption of the Langmuir adsorption isotherm. Obtain a statistical expression of a Langmuir adsorption isotherm. 2+5=7

UNIT—III

5. Considering the equilibrium between a system and particle-energy reservoir, deduce an expression for partition function and henceforth, arrive at an expression of B-E statistics. 8+6=14

6. *(a)* Derive an expression for number of particles at the ith level (n_i) considering classical distribution. 11

(b) Show that the energy of a system of ideal non-interacting bosons is less than that of a classical gas at the same temperature and volume. 3

UNIT—IV

7. *(a)* Determine the molecular weight of a polymer using osmometry method. 7

(b) Explain the optical and geometrical isomerism exhibited by polymers with suitable examples. 7

8. *(a)* Explain the kinetics of free radical and ionic polymerization with examples and distinguish the important features. 10

(b) Define number average molecular weight and weight average molecular weight. What is polydispersity index of a polymer sample? 4

UNIT—V

9. *(a)* Derive an expression for Langmuir adsorption isotherm for surface reactions without dissociation and competitive adsorption. 7

(b) Discuss the statistical treatment of adsorption of an ideal gas. 7

10. *(a)* Explain bimolecular surface reaction based on Langmuir-Hinshelwood mechanism and elucidate how an inhibitor affects the rate in bimolecular surface reaction. 8

(b) Draw the potential energy diagram for a unimolecular surface reaction and discuss the observed activation energy for the reaction. 6

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