PG Odd Semester (CBCS) Exam., December—2017

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)* What are ensembles? How are they classified? State the fundamental postulates of 'ensemble averaging'. 1+1+3=5

(b) Using the microcanonical approach, how can the concept of temperature be introduced? 9

2. *(a)* Using rigid rotor approximation for diatomic molecule, obtain an expression of rotational partition function at low- and high-temperature limit. 3+3=6

(b) Calculate the rotational partition function for the molecule HD at 298·15 K. Given that the moment of inertia for HD is $6\ 29\ \ 10^{\ 48}$ kg m^2. Compare their classical and quantum results. 2+2=4

(c) Obtain an expression relating translational partition function of ideal monoatomic gas with the thermodynamic functions : 2+2=4

(i) Energy

(ii) Entropy

UNIT—II

3. *(a)* Obtain an expression relating the electronic partition function of monoatomic gas with their thermodynamic functions : 2+2=4

(i) Molar energy

(ii) Entropy

(b) The ground electronic level of O-atom is five-fold degenerate and the subsequent first two higher levels have degeneracies of 3 and 1 respectively. The energies corresponding to the ground level and the first two excited level are 0, 158·5 and 226·5 cm ^{1} respectively. From these data, calculate the population of this electronic level of O-atom at 25 °C.

[Given, 1 eV =
1 6 10 ^{12} erg 8 066 10 ^{13} cm ^{1}]

Boltzmann constant,
k_b 1 38 10 ^{16} erg K ^{1} mole ^{1} 4

(c) Consider a gas phase reaction

$$_A A \quad _B B \rightleftharpoons \ _C C \quad _D D$$

's stoichiometric coefficient of reactant *A*, *B* and product *C*, *D* respectively. Obtain an expression of equilibrium constant with partition function. 6

4. *(a)* Association of alkali metal vapours

$$2Na \rightleftharpoons Na_2$$

at high temperature, they are stable. Find $k_p(I)$ at 1000 K.

[Given, $_v$ 229 K; $_r$ 0 22 K
D_o 17 3 kcal mol ^{1}
1 kcal/mol = 6 95 10 ^{14} erg
1 atm = 1 01 10^6 dynes cm ^{2}] 5

(b) Discuss the basic assumption of Einstein theory of specific heat of solid. Obtain an expression of heat capacity of the solids. Discuss the results of high- and low-temperature limit. 2+4+3=9

UNIT—III

5. *(a)* Considering closed-isothermal system, deduce an expression for Maxwell-Boltzmann distribution law. 12

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

6. Considering the equilibrium between a system and particle-energy reservoir, deduce an expression for partition function and henceforth, arrive at an expression for Fermi-Dirac statistics. 9+5=14

UNIT—IV

7. *(a)* Describe the light scattering method for the determination of molecular weight of macromolecules. 8

(b) Write short notes on the following : 3×2=6

(i) Optical isomerism in macromolecules

(ii) Emulsion polymerization in solution

8. *(a)* Explain the kinetics of free radical and anionic polymerization with examples. 8

(b) Write short notes on the following : 3×2=6

(i) Geometrical isomerism in macromolecules

(ii) Average molecular weight of a polymer

UNIT—V

9. *(a)* Draw the potential energy diagram for a unimolecular surface reaction and discuss the observed activation energy for the reaction changes from low pressure to high pressure. 8

(b) Use Langmuir-Hinshelwood mechanism to explain the hydrogenation of ethylene on a surface reaction. 3

(c) Explain bimolecular surface reaction based on Langmuir-Rideal mechanism. 3

10. *(a)* Discuss the statistical treatment of adsorption of an ideal gas. 5

(b) Elucidate how an inhibitor affects the rate in bimolecular surface reaction. 3

(c) Derive the expression for Langmuir adsorption isotherm for surface reaction with and without dissociation. 6

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