

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

CHEMISTRY

(3rd Semester)

Course No. : CH-303 (C)

(Physical Chemistry—III)

Full Marks : 75Pass Marks : 30

Time : 3 hours

*The figures in the margin indicate full marks
for the questions*

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

UNIT—I

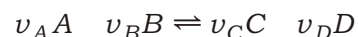
1. (a) What are ensembles? How are they classified? Using micro-canonical approach, how can the concept of temperature be introduced? 1+2+5=8
- (b) State the fundamental postulates of ensemble averaging. 4
- (c) The molar entropy of He at a given temperature and pressure is 30.1 eV. What is the molar entropy of Ne (at. wt = 20.2 a.u.) at the same temperature and pressure? 3

2. (a) What is phase space? Derive translational partition function of a particle in a 3D box by using classical energy. 2+5=7
- (b) If entropy $S = k \sum_i p_i \ln p_i$, obtain relation for E and A in terms of partition function (Q) , using microcanonical ensembles distribution law. 2+2=4
- (c) "Rotational characteristic temperature can be used to determine the bond length of a diatomic molecule." Explain. 4

UNIT—II

3. (a) By considering a one-dimensional quantum mechanical simple harmonic oscillator, find out the expression for partition function and show that this expression in the high temperature limit, give the same expression as obtained for a classical oscillator. 6
- (b) Find out an expression for heat capacity of an Einstein crystal. What does this expression yield at high temperature? 6
- (c) Explain electronic partition function (q^E) is usually just equal to degeneracy of the electronic ground state. 3

4. (a) Derive an expression for $k_p(T)$ for the homogenous gas phase chemically reaction



in terms of molar partition functions of species A, B, C and D. 9

- (b) Determine the equilibrium constant of association of alkali metal vapour $2\text{Na} \rightleftharpoons \text{Na}_2$ at 1000 K. Given that the dissociation energy, vibrational temperature and rotational temperature are $17.3 \text{ kcal mol}^{-1}$, 229 K and 0.221 K respectively. The next electronic state lies approximately 16000 cm^{-1} above the ground state. 6

UNIT—III

5. (a) 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. 9
- (b) What are the characteristics of the quantum particles (i) bosons and (ii) fermions? 2
- (c) What are the conditions under which B-E and F-D statistics approach Boltzmann statistics? 4

6. (a) Considering closed isothermal system, deduce an expression for Maxwell-Boltzmann distribution law. 10
- (b) Assuming the form of probability distribution function of a given canonical ensemble, how can we arrive to the B-E distribution function? 5

UNIT—IV

7. (a) How is the particle scattering factor related to the size of polymer molecules? Explain how the molecular weight of a polymer solution can be determined from light scattering data. 8
- (b) Explain free radical polymerization with an example. 7
8. (a) Describe with relevant expressions the sedimentation method of determining average molecular weight of macromolecules. 7
- (b) Explain with examples optical and geometrical isomerism in macromolecules. 4+4=8

UNIT—V

9. (a) Explain bimolecular surface reaction based on Langmuir-Hinshelwood mechanism and elucidate how an inhibitor affect the rate in a bimolecular surface reaction. 8
- (b) Draw the potential energy diagram for a unimolecular surface reaction and discuss the observed activation energy for the reaction. 7
10. How many mechanisms are there to explain the bimolecular surface reactions? Discuss the kinetics of bimolecular surface reactions in the light of the following specific situations : $2+3+3+3+2+2=15$
- (a) Reaction between two adsorbed molecules
- (b) Reaction between a gas molecule and an adsorbed molecule
- (c) Adsorption of two gases without mutual displacement
- (d) Inhibition
- (e) Activation energies
