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

CHEMISTRY

(3rd Semester)

Course No. : CH–303 (C)

(Physical Chemistry—III)

Full Marks : 75
Pass 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 $S \quad k \quad \underset{i}{} p_i \ln p_i$, 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

$$\upsilon_A A \quad \upsilon_B B \rightleftharpoons \upsilon_C C \quad \upsilon_D D$$

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 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

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