PG Odd Semester (CBCS) Exam., December—2018

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)* State the fundamental postulates of ensemble averaging. Draw the phase space diagram of a particle in one-dimensional box. 2+2=4

(b) Show that $|nN|$ $N|nN$ N, when N is very large. 3

(c) Assuming a canonical ensemble, show that fluctuation in average value of energy decreases as the number of particles in the ensemble increases. 7

2. *(a)* By using the concept of phase space, obtain an expression for translational partition function of N indistinguishable particles. 7

(b) What is the energy required to excite an H-atom (m 1 674 10^{24} g) in a cubic box of volume 1 m^3 from the ground state (n_x 1, n_y 1, n_z 1) to the first excited state (n_x 2, n_y 1, n_z 1)? Calculate translational partition function for an oxygen molecule (molecular weight 31·99 g mol^{1}) at 273·15 K when occupying a volume of 22·414 dm^3. 3

(c) The rotational motion of diatomic molecules can be approximated by a quantum mechanical rigid rotor assuming that the moment of inertia of a diatomic molecule is 10^{40} gm cm^2. Calculate the partition function of first five rotational levels of a diatomic ideal gas at 25 °C. (Consider high temperature limit for rotational partition function.) 4

UNIT—II

3. *(a)* Derive statistically Langmuir adsorption isotherm of ideal gas. 9

(b) Find out the $k_C(T)$ for ionization of H-atom. 5

4. *(a)* Using HO model, obtain an expression for vibrational partition function. 5

(b) Show that at high temperature, vibrational partition function, $Q_{\text{vib}} \quad \frac{kT}{h \ \nu}$. 3

(c) Consider a system of independent diatomic molecules moving on a plane, i.e., 2D ideal diatomic gas. Given that the rotational energy of a two-dimensional gas is $_J \quad \frac{\hbar^2 J^2}{2I}$, where $\hbar \quad h/2$; $J \quad 0, 1, 2, 3, \cdots$; $I \quad r^2$ with a degeneracy factor $J_J \quad 2$ for all J. Calculate the rotational partition function. The vibrational partition function is the same as for a 3D diatomic molecule. Write $Q_{\text{rot}} \quad Q_{\text{vib}} \quad Q_{\text{tr}}$ and derive expression of energy for this ideal 2D diatomic gas. 6

UNIT—III

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

(b) Six distinguishable particles are distributed over three non-degenerate levels of energies 0, and 2 . Calculate the total number of microstates in the system. 2

6. *(a)* Assuming the concept of grand canonical ensemble, deduce an expression for the partition function and henceforth, arrive at an expression of Fermi-Dirac statistics. 7+5=12

(b) What are the characteristics of quantum particles *(i)* bosons and *(ii)* fermions? 2

UNIT—IV

7. *(a)* Explain the kinetics of free radical and cation polymerization with example and distinguish the important features. 4+4=8

(b) Give a brief account of optical and geometrical isomerism in macro-molecules with examples. 4

(c) Equal masses of polymer molecules with $M_1 \quad 10000$ and $M_2 \quad 100000$ are mixed. Calculate $\overline{M}_N$ and $\overline{M}_m$. 1+1=2

8. *(a)* Determine the molecular weight of a polymer using osmometry method. 6

(b) Describe the light scattering method for the determination of molar masses of macromolecules. 6

(c) The following data were obtained on the osmotic pressure of solutions of globulin in 0·15 *M* NaCl at 37 °C :

C, g/100 ml	19·27	12·53	5·81
, mm H_2O	453	253	112

Calculate the molar mass of the polymer. 2

UNIT—V

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

(b) 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. 5

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

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

(b) Discuss the kinetics of bimolecular surface reactions in the light of the following specific situations :

(i) Reaction between two adsorbed molecules

(ii) Reaction between a gas molecule and an adsorbed molecule

(iii) Adsorption of two gases without mutual displacement 6

(c) The data given below are for the adsorption of CO on charcoal at 273 K. Confirm that they fit the Langmuir isotherm and find the constant *K* and the volume corresponding to complete coverage. In each case *V* has been corrected to 1·00 atm : 3

P/kPa	13·3	26·7	40·0	53·3	66·7	80·0	93·3
V/cm^3	10·2	18·6	25·5	31·5	36·9	41·6	46·1

★ ★ ★