(c) Calculate the molar mass of haemoglobin from the fact that in the sedimentation equilibrium experiment at 20 °C, C_2/C_1=9.40, r_1 =5.5 cm and r_2 = 6.5 cm. The ultracentrifuge rotor is operated at 120 rps. $\bar{v} = 0.749 cm^3 g^{-1}$ and ρ=0.9982 gm cm^{-3}. 3

UNIT - V

9. (a) Derive an expression for Langmuir adsorption isotherm for surface reactions 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 the Langmuir-Hinshelwood mechanism to explain the hydrogenation of ethylene on a surface reaction. 4

10. (a) Explain in detail the statistical treatment of adsorption. 5

(b) 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:

(i) Reaction between two adsorbed molecules

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

(iii) Adsorption of two gases without mutual displacement 3+3+3 = 9

★★★

PG (CBCS) ODD SEMESTER EXAMINATION, 2022

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 any five questions, taking one from each unit)

UNIT - I

1. (a) What is ensemble? Write down the two postulates of ensemble averaging. 1+4 =5

(b) What is Partition function? Write down the general relationship of partition function with the following thermodynamics function
(i) molar energy (ii) molar entropy (particles are indistinguishable) (iii) Pressure 1+2+4+2 =9

2. (a) Obtain an expression for the rotational partition function for an ideal diatomic molecule using rigid rotor model by considering two extreme temperature limits. 7

(b) Calculate the rotational partition function for the molecule at 298.15 K. Given that the moment of inertia for HD is 6.29 x 10-48 Kg^2. [Use Planck's constant, h = 6.626 x 10^{-34}Js and Boltzman constant k = 1.388x10-23 JK^{-1}]. 3

(c) Calculate the molar entropy of argon gas (M = 39.948 $gmol^{-1}$) at 298.15 K and 1 bar of pressure (1 bar = 10^5 Pa; 1 Pa = $1Nm^{-2}$). 4

UNIT - II

3. (a) By considering the vibrational partition function at ambient temperature, obtain an expression for the heat capacity of a diatomic molecule. Discuss the heat capacity when T tends to infinity and T tends to zero 3+2+2 =7

(b) Justify the statement "The electronic partition function is usually just equal to the degeneracy of the electronic state". 4

(c) What will be the fraction of He- atom in the lowest triplet state $^3s_1$ at 300 K and 3000 K. Discuss the result. (Assume triplet energy state, E_2 = 19.8 eV) 3

4. (a) By using a concept of partition function, derive an expression for Langmuir adsorption isotherm by considering ideal lattice gas. 8

(b) Discuss the assumptions of Einstein theory of specific heat of solid, Obtain an expression for the specific heat of a solid. 6

UNIT - III

5. Show that the equilibrium distribution of particles following Bose-Einstein statistic is given by

$$N_i = \frac{g_i}{e^{-\alpha} e^{\beta \varepsilon_i} - 1}$$

Where α and β are constant. Also, show that for a system in which $g_i/N_i \gg 1$, the equilibrium distribution can be computed by using Boltzmann distribution law. 9+5 = 14

6. Show that the equilibrium distribution of particles following Fermi-Dirac statistic is given by

$$N_i = \frac{g_i}{e^{-\alpha} e^{\beta \varepsilon_i} + 1}$$

Where α and β are constant. Also, show that for a system in which $g_i/N_i \gg 1$, the equilibrium distribution can be computed by using Boltzmann distribution law. 9+5 =14

UNIT - IV

7. (a) What is meant by number-average molar mass and weight average molar mass of a Polymer? What is the polydispersity index of a polymer sample? 3+2=4

(b) Write the stepwise reaction mechanism and drive the rate expression of radical polymerization. 5

(c) Discuss the effects of chain transfer agents in polymerization? What is Mayo equation? 2+2=4

8. (a) Distinguish between the isotactic, syndiotactic, and atactic polymers. 3

(b) Describe the light scattering method for the determination of molar mass of macromolecules. Draw the Zimm plot. 6