3 Yr. Degree/4 Yr. Honours 5th Semester Examination, 2025 (CCFUP)

Subject : Chemistry

Course : CHEM 5013 (MAJOR)

(Physical Chemistry)

Time: 2 Hours **Full Marks: 40**

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

1. Answer *any five* questions: 2×5=10

(a) What is the lowest possible value of thermodynamic probability and why?

(b) 'Adsorption is always exothermic'.— Comment.

(c) Boltzman distribution law is expressed as:

$N_i = N g_i e^{\alpha} e^{-\beta \varepsilon i}$. Find e^{α}

[Given: N = total number of particles, N_i = number of particles in the ith energy level. Other terms have their usual meaning.]

(d) Give the final form of Gibb's adsorption isotherm with the meaning of different symbols used.

(e) What is Gibbs paradox in the entropy of mixing of ideal gases and how did Gibbs resolve it?

(f) Write down the unit and dimension of 'angular momentum'.

(g) Find out the intercepts on the crystallographic axes of a plane with Miller indices (2 0 1) with unit cell dimensions a = 6.8 nm, b = 8.6 nm and c = 4.6 nm.

(h) Write down the relationship between extent of reaction and degree of polymerization with meaning of each terms involved.

2. Answer *any two* questions: 5×2=10

(a) (i) What do you understand by the term 'space quantization of angular momentum'?

(ii) Derive the relation: $\sqrt{[J(J+1)]}\cos\theta = m_z$ (terms have their usual meaning) and hence show that the angle θ can have only a few permitted values. 1+(2+2)

(b) (i) Write short notes on [a] Schultz-Hardy rule and [b] Zeta potential

(ii) What is meant by the term 'functionality' in polymer science? (2+2)+1

(c) (i) Derive the Langmuir adsorption isotherm with graphical plot.

(ii) What does the statement 's-orbitals are spherically symmetric'? Signify. 3+2

(d) (i) Why are the numbers 6, 6 and 6 put in the names of nylon-6, 6 and nylon-6?

(ii) Write down the differences between thermosetting and thermoplastic polymers. Give examples for each type also. 2+3

3. Answer *any two* questions: 10×2=20

(a) (i) For a particle of mass 'm' moving in a cubical box of side length 'a', determine the total energy and the degree of degeneracy of the level characterized by $n_x + n_y + n_z = 6$.

(ii) Define the terms 'chemisorption' and 'physisorption' with examples.

(iii) Molar polarization of water molecule varies inversely with temperature.— Comment.

(iv) Define canonical ensemble. 4+3+2+1

(b) (i) Depict schematically the normalized harmonic-oscillator wavefunctions and corresponding probability densities for the first two states of a SHO.

(ii) Derive the rate law for step-growth polymerization process in presence of an external acid catalyst.

(iii) Express the internal energy of a system of N non-interacting particles in terms of its molecular partition function. 3+4+3

(c) (i) A sample of polymer consists of 10% by weight of polymer of molecular weight 15000 and 90% by weight of polymer of molecular weight 150000. Find out the polydispersity index of the polymer.

(ii) What are the methods of determining the molecular weights of polymer?

(iii) For HCl, the measured dipole moment is 1.04 Debye and the bond length is 1.275 Å. Calculate the % ionic character in HCl.

(iv) Why are radio waves unsuitable for determining crystal structure? 3+2+3+2

(d) (i) Calculate the percentage of void space in a FCC lattice.

(ii) A compound formed by elements A and B crystallizes in the cubic arrangement in which atoms A are at the corners of the cube and atoms B are at the face centers. What is the formula of the compound?

(iii) Lithium metal has BCC structure. It has a density of 0.53 g cm^{-3} and molar mass 6.94 g mol^{-1}. Calculate the wavelength of the X-ray that will produce a 2nd order reflection from the (121) plane at a glancing angle of 10.3°.

(iv) List the different axes of symmetry present in a cube. 3+2+3+2
