B.Sc. 5th Semester (Honours) Examination, 2022 (CBCS)

Subject: Chemistry

Course: DSE-1

(Advanced 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:

 $2 \times 5 = 10$

- (a) How are polymers classified on the basis of their structure? Discuss with examples.
- (b) Boltzman distribution law is expressed as:

 $N_i = N g_i e^{\alpha} e^{-\beta \in i}$. 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.]

- (c) Find the percentage error in calculation of ln(8!) using Stirling's approximation.
- (d) What is vulcanization? How it is done.
- (e) Explain why some system have nonzero entropy value even at 0K, citing proper example.
- (f) What is the minimum measurable value of spacing between crystal planes when the wavelength of 1.67Å is employed?
- (g) Can a molecule with zero dipole moment undergo polarization? Justify your answer.
- (h) Why are radio waves considered to be unsuitable for determining crystal structure?

2. Answer *any two* questions:

 $5 \times 2 = 10$

- (a) (i) Give one example each of (a) addition polymer, (b) condensation polymer, (c) copolymer mentioning the type of polymerization reaction and starting materials in each case.
 - (ii) Determine the molecular weight of a polystyrene sample which has an α (alpha) value of 0.60, K value of 104 dl/gm and a limiting viscosity number (or intrinsic viscosity) of 0.04 dl/gm.
- (b) (i) State and explain Nernst heat theorem.
 - (ii) Show that the heat capacity would remain unchanged in any transformation in the vicinity of 0K.
 - (iii) What is meant by the term 'functionality' in polymer science?

2+2+1

- (c) (i) Consider an isolated system composed of 3 distinguishable particles. Calculate the possible ways of distributing the 3 distinguishable particles of the isolated system among 4 energy levels with energies 0, €, 2 € and 3 €, respectively. The total energy of the system remains constant at 4 €. (No restriction on the number of particles in any energy level).
 - (ii) Calculate the entropy of the above system as mentioned in 2.c (i) at an equilibrium. 3+2

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- (d) (i) Why the numbers 6, 6 and 6 are put in the name of nylon-6, 6 and nylon-66, respectively?
 - (ii) What are thermosetting and thermoplastic polymers? Give examples for each.

3. Answer *any two* questions:

 $10 \times 2 = 20$

3+2

- (a) (i) Derive an expression for molar heat capacity (C_v) of a monoatomic solid according to Einstein model.
 - (ii) Show that for a Boltzman distribution $N_i \ge N_{i+1}$. When do the equality sign hold?
 - (iii) Molar polarization of water molecule varies inversely with temperature. Comment.
 - (iv) Define canonical ensemble.

4+3+2+1

- (b) (i) Consider a two-level system where the energy difference between the ground state and first excited state is 3.139×10^{-20} J. At what temperature would the first excited state have the half of the population of the ground state?
 - (ii) Arrange the following molecules in order of increasing standard molar entropy at a certain temperature: $C_2H_6(g)$, $C_2H_4(g)$, $C_2H_2(g)$. Explain your answer.
 - (iii) Calculate the number of microstates for a system containing three energy state with configuration of (2, 1, 0). Show all the schematic representation.
 - (iv) Define partition function. Predict the value of such parameter when $T \to 0$ and $T \to \infty$. 2+2+3+3
- (c) (i) Insulin forms crystals of orthorhombic type with a = 13 nm, b = 7.48 nm and c = 3.09 nm. If the density of the crystal is 1.315×10^3 kg/m³, and there are 66 insulin molecules per unit cell. What is the molar mass of insulin?
 - (ii) 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.
 - (iii) The distance between two successive parallel planes in a cubic crystal cannot be $a/\sqrt{7}$ comment. (a = length of the edge of the cube).
 - (iv) State Debye T³ law and mention its utility.

3+2+2+3

- (d) (i) Ag is known to crystallise in f.c.c. form and the distance between the nearest neighbour atoms is 2.87 Å. Calculate the density of Ag [At. Wt. of Ag = 108].
 - (ii) Derive the rate law for step-growth polymerization process.
 - (iii) Give the idea and two examples of conducting polymer.
 - (iv) Point out viscosity average molecular weight (M_v) , weight average molecular weight (M_w) and number average molecular weight (M_n) in graphical variation of weight fraction vs. molecular weight. 3+2+3+2