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: 2×5=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: 5×2=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 d*l*/gm and a limiting viscosity number (or intrinsic viscosity) of 0·04 d*l*/gm. 3+2

(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, $\in$, 2$\in$ and 3$\in$, respectively. The total energy of the system remains constant at 4$\in$. (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

(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+2

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

(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 $N_i \geq N_{i+1}$. 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 $3{\cdot}139 \times 10^{-20}$ 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 $T \rightarrow 0$ and $T \rightarrow \infty$. 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 $1{\cdot}315 \times 10^3$ kg/m^3, 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 T^3 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