B.Sc. 5th Semester (Honours) Examination, 2023 (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) Name the different types of Bravais lattices that can be obtained for a tetragonal crystal. Find the number of atoms per unit cell for a body-centred tetragonal crystal.

(b) Mention two differences between tetrahedral void and octahedral void.

(c) Define microcanonical ensemble. What type of thermodynamic system is defined by it?

(d) Show that the barometric pressure distribution is a special case of the Boltzman distribution.

(e) The bond moment of H_2S molecule is 1·11D and the bond angle is 97°. Find the dipole moment of H_2S molecule.

(f) Distinguish between thermoplastic polymer and thermosetting polymer.

(g) Why does molar polarization of polar molecule decreases at high frequencies?

(h) Define vibrational temperature of a system. What is its unit?

2. Answer *any two* questions: 5×2=10

(a) (i) The molar volume of KCl is 1·3 times that the NaCl. The glancing angle for the 1st order Bragg reflection from the (200) plane of NaCl is 5·9°. Find the glancing angle from the (200) plane of KCl.

(ii) Define partition function for a degenerate system. Find the significance of it at T = 0K. 3+2

(b) (i) Calculate the percentage of space occupied in an atomic BCC lattice.

(ii) For macromolecules, show that $\bar{M}_w \geq \bar{M}_n$. 3+2

(c) (i) Entropy is additive whereas thermodynamic probability is multiplicative. Hence, arrive at the Planck's relation $S = k \ln W$.

(ii) Find the number of microstates for the distribution of 4 indistinguishable particles in 5 boxes. 3+2

(d) (i) For the distribution of N distinguishable molecules in different energy levels, where n_i molecules present in energy level ϵ_i (non-degenerate), show that $S = -Nk \sum P_i \ ln \ P_i$, where P_i is the probability of finding the molecules in the ith states.

(ii) Show a plot of C_P/T vs. T in accordance with the Third law. What is the meaning of area under this curve? 3+2

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

(a) (i) Derive the Bragg's equation of diffraction of X-ray on a crystal. State the condition for the validity of this equation.

(ii) In X-ray diffraction, KCl shows SC pattern though it is a FCC lattice. —Comment.

(iii) For equispaced energy levels, show that the population in the middle level is the geometric mean of the populations of its immediate upper and lower level.

(iv) Write down the Clausius–Mossotti equation for a polar molecule explaining the terms involved within it. Find the unit of Molar polarization from this equation. 3+2+3+2

(b) (i) Find an expression of Helmholtz's function in terms of the molecular partition function.

(ii) Derive an expression of translational partition function. Hence show that $U_{trans} = \frac{3}{2}RT$ per mole for an ideal gas.

(iii) Aluminium (At. wt. 27, density 2·69 g cm^{-3}) crystallises with FCC lattice. What is the distance of closest approach of Al-atoms in the crystal. 3+4+3

(c) (i) Find an expression of vibrational partition function in case of a Harmonic oscillator.

(ii) If the molecular partition function Q of a gaseous system is given by $Q = \exp(A + B\ ln\ T)$, where A and B are constants; then find the expression for the molar heat capacity (C_V) of the gas. Hence show that for a monoatomic ideal gas, $B = \frac{3}{2}N_A$, where N_A = Avogadro No. Given $U = NkT^2\left(\frac{\partial\ ln\ Q}{\partial T}\right)_{V,N}$.

(iii) The dipole moment of chlorobenzene is 1·55 D. The bond distance of C_6H_5 — Cl is 2·8 Å. Calculate the ionic character. 3+(3+2)+2

(d) (i) Find the partition function for two-level system, where the lower state (at energy 0) is non-degenerate and the upper state is doubly degenerate (at energy ϵ). Take $\epsilon = 2kT$.

(ii) What is Gibbs paradox? State the theoretical justification by which the paradox is resolved.

(iii) A solid containing 4 number of atoms, melt. What will be its effect in the partition function?

(iv) Find the integrated rate equation of a condensation polymerization reaction in presence of a mineral acid in terms of extent of polymerization. 2+3+2+3

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