

## 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

- 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.
- Mention two differences between tetrahedral void and octahedral void.
- Define microcanonical ensemble. What type of thermodynamic system is defined by it?
- Show that the barometric pressure distribution is a special case of the Boltzmann distribution.
- The bond moment of  $\text{H}_2\text{S}$  molecule is 1.11 D and the bond angle is  $97^\circ$ . Find the dipole moment of  $\text{H}_2\text{S}$  molecule.
- Distinguish between thermoplastic polymer and thermosetting polymer.
- Why does molar polarization of polar molecule decreases at high frequencies?
- Define vibrational temperature of a system. What is its unit?

2. Answer any two questions:

5×2=10

- The molar volume of KCl is 1.3 times that of NaCl. The glancing angle for the 1st order Bragg reflection from the (200) plane of NaCl is  $5.9^\circ$ . Find the glancing angle from the (200) plane of KCl.
  - Define partition function for a degenerate system. Find the significance of it at  $T = 0\text{K}$ .
- Calculate the percentage of space occupied in an atomic BCC lattice.
  - For macromolecules, show that  $\bar{M}_w \geq \bar{M}_n$ .
- Entropy is additive whereas thermodynamic probability is multiplicative. Hence, arrive at the Planck's relation  $S = k \ln W$ .
  - Find the number of microstates for the distribution of 4 indistinguishable particles in 5 boxes.
- For the distribution of  $N$  distinguishable molecules in different energy levels, where  $n_i$  molecules present in energy level  $\epsilon_i$  (non-degenerate), show that  $S = -Nk \sum P_i \ln P_i$ , where  $P_i$  is the probability of finding the molecules in the  $i$ th states.
  - 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. Answer any two questions:

- (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  $2.69 \text{ g cm}^{-3}$ ) 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  $\text{C}_6\text{H}_5 - \text{Cl}$  is  $2.8 \text{ \AA}$ . 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  $\epsilon$ ). 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