

B.Sc. 5th Semester (Honours) Examination, 2019 (CBCS)**Subject : Chemistry****Paper : DSE-I****(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) What is meant by a 'tetragonal class of crystal? Find the number of atoms per unit cell for a body-centred tetragonal crystal.
 - (b) Distance between two Miller planes cannot be $a/\sqrt{7}$ in case of a cubic crystal system — comment.
 - (c) Define vibrational temperature of an ideal gas. What is its unit?
 - (d) Show that heat capacity would remain unchanged in any transformation, in the vicinity of 0 K.
 - (e) Write the Partition function for a two-level system, where the lower state (at energy 0) is non-degenerate and the upper state (at energy ϵ) is doubly degenerate.
 - (f) Distinguish between thermoplastic polymer and thermosetting polymer.
 - (g) Write down the Boltzmann distribution for a degenerate system stating the terms involved in the equation.
 - (h) Why does molar Polarisation of a Polar molecule decrease at high frequencies?
2. Answer *any two* questions: 5×2=10
 - (a)
 - (i) Five-fold rotational axis of symmetry is impossible in case of a crystal. Justify.
 - (ii) A system is with four energy levels having population (3, 2, 1, 0) of six particles. Calculate the entropy of the system. 3+2=5
 - (b)
 - (i) Show that the barometric pressure distribution is a special case of the Boltzmann distribution.
 - (ii) By means of lattice diagram, show the possible Bravais lattices in case of an orthorhombic system of crystals.
 - (iii) Define a 'canonical ensemble'. 2+2+1=5
 - (c)
 - (i) State the Principle of determination of mol. wt. of a Polymer sample with the help of viscometry.
A polydisperse protein has 10% of molecules of mol. wt. 10,000, 80% of 20,000 and 10% of 40,000. Calculate the mass average mol. wt. of the protein.
 - (ii) Predict the statistical entropy of an ideal gas at $T \rightarrow 0$. (2+2)+1=5

- (d) (i) Show that the distance of separation between the successive hk -planes in a two dimensional square lattice is $\frac{a}{\sqrt{h^2+k^2}}$, where 'a' is the unit distance along X and Y axes.
- (ii) The residual entropy of carbon monoxide is about $5.76 \text{ JK}^{-1} \text{ mol}^{-1}$. — Comment. 3+2=5

3. Answer any two questions:

10×2=20

- (a) (i) Define partition function. What is its unit? The molecular partition function of an ideal monatomic gas is given by $q = \left(\frac{AT}{B}\right)^{\frac{3}{2}} V$, where A and B are constants and other terms have their usual significance. Find the expressions of molar internal energy and pressure of the gas.
- (ii) Calculate the barometric pressure at an altitude of 10 km for air considering barometric pressure at sea level is 760 torr and average molar mass of air is $28.8 \times 10^{-3} \text{ kg mol}^{-1}$ at a constant temperature of 27°C .
- (iii) Polymers are also known as molecular colloids. Why? [(1+1)+3]+3+2=10
- (b) (i) Silver is known to crystallize in FCC form and distance between the nearest neighbours is 2.87\AA . Calculate the density of Silver. [Atomic weight of Ag is 108]
- (ii) Explain the difference between induced and orientation polarization. Which one is temperature dependent and why?
- (iii) Sketch Debye plots to show the expected variation of the molar polarisation for gaseous HF, HCl, and HBr, with $1/T$. Comment on the relative slopes and intercepts of the lines drawn. 4+(2+1)+(1+2)=10
- (c) (i) Define 'residual entropy'. Find an expression of Helmholtz function A in terms of partition function.
- (ii) Deduce an expression of translational partition function of an ideal gas.
- (iii) In X-ray analysis, KCl shows simple cubic type though it is FCC type like NaCl. — Why?
- (iv) Show that $\bar{M}_w \geq \bar{M}_n$ in case of polymers. (1+2)+3+2+2=10
- (d) (i) Derive an expression of vibrational partition function for a Planck's oscillator (classical). Hence arrive at the Einstein's expression of molar heat capacity of a monatomic solid. Comment on its value at low and high temperature limit.
- (ii) What is Gibbs paradox?
- (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\AA . Estimate the ionic character of the bond. (2+2+2)+2+2=10