

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:

$10 \times 2 = 20$

- (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 $C_6H_5 - Cl$ is 2.8\AA . Estimate the ionic character of the bond. $(2+2+2)+2+2=10$
-