

B.Sc 5th Semester(Honours) Examination 2021 (CBCS)

Subject: Chemistry

Advanced Physical Chemistry

Paper: DSE – 1

Time : 2 Hours

Full marks : 40

[Candidates are requested to give their answers in their own words as far as practicable]

Answer any eight questions from following: $5 \times 8 = 40$

1. Give brief scientific explanation behind correlation of thermodynamic entropy(S) with thermodynamic probability(W). Establish the functional relationship between S and W.

2. What is the key difference between *hcp* and *ccp* structures? Suppose X atoms form a close packed lattice structure, where Y atoms (smaller than X atoms) have to be incorporated without disturbing the close-packed lattice. Write down the formula of the compounds with proper justification when (i) Y atoms are occupied in all tetrahedral voids; (ii) Y atoms are occupied in half of the tetrahedral voids; (iii) Y atoms are occupied in all the octahedral voids; and (iv) Y atoms are occupied in half of the octahedral voids. Mention the limiting radius in each case of Y atoms in regard to that of X atoms, so that Y atoms fit perfectly either in tetrahedral voids or in octahedral voids.

3. (a) Europium (Atomic weight: $152 \text{ g} \cdot \text{mol}^{-1}$) crystallizes in a *bcc* lattice. The density of Europium (Eu) is estimated to be $5.26 \text{ g} \cdot \text{cm}^{-3}$. Calculate the radius of Eu atom from above information.

(b) Determine the highest order of reflection that can be observed in Bragg's reflection from a solid employing X-ray spectroscopic technique.

4. Consider nine number of molecules divided equally in three non-degenerate energy levels. What is the thermodynamic probability (W) for this distribution? How does the value of W change if two number molecules are removed from one of the energy level and then one molecule is added subsequently each to the remaining two levels? Also calculate the difference of entropy between the two distributions.

5. Define partition function(*f*) according to Maxwell-Boltzman distribution mentioning all the terms involved in it. Comment on the value of *f* as Temperature $\rightarrow \infty$.

Comment: While energy is additive, *f* is multiplicative in its nature.

6. What is Copolymerisation? Give suitable reason(s) behind the purpose of Copolymerisation citing proper instances. Mention the different types of copolymers. Write down the molecular formula of nylon-66 along with the name(s) and molecular formula(s) of the monomeric units involved in such process.

7. Derive the Carother's equation relating average functionality (q_{av}), extent of reaction (P) and average degree of polymerization (\bar{X}_n) for a polycondensation reaction. From it, arrive at the expression of average degree of polymerization (\bar{X}_n) for the formation of a strictly linear polymer by carrying out the reaction between two monomer units in equimolar quantity.

8. The Lennard-Jones potential (ϵ) $\epsilon = -(A/r^6) + (B/r^n)$ may be expressed in terms of ϵ_m , the energy at the minimum, and r_0 , the distance of separation at the minimum. Find A and B in terms of r_0 , ϵ_m , and n . If σ is the distance of separation when $\epsilon = 0$, find the relation between r_0 and σ .

9. Crystals of H_2O have a residual entropy of $3.35 \text{ J K}^{-1} \text{ mol}^{-1}$ at 0K – Explain.

$\lim_{T \rightarrow 0} (C_p - C_v) \rightarrow 0$ – Establish from 3rd law of thermodynamics.

$T \rightarrow 0$

10. (a) Write down the drawback of Einstein's equation of heat capacity of solids. Mention the main difference between the assumptions of Einstein and that of Debye regarding the vibrations in solids.

(b) Designate the *Miller* indices of all the six faces of a simple cubic unit cell with appropriate diagram.
