

U.G. 6th Semester Examination - 2025**CHEMISTRY****[HONOURS]****Discipline Specific Elective (DSE)****Course Code : CHEM-H-DSE-T-3****(Advanced Physical Chemistry)**

Full Marks : 40

Time : $2\frac{1}{2}$ Hours*The figures in the right-hand margin indicate marks.**Candidates are required to give their answers in their own words as far as practicable.*

1. Answer any five questions: 2×5=10
- i) Miller indices indicate a set of parallel planes—
Comment.
 - ii) Find the effective number of atoms for an hcp unit cell.
 - iii) What do you mean by degenerate state and degeneracy of state?
 - iv) What important information can be found from the Nernst heat theorem?

[Turn Over]

v) The supply of the same amount of heat will not increase the temperature of a substance to the same extent at 10K and 100K- Comment.

vi) Spontaneous polymerisation is an exothermic process—Explain.

2. Answer any two questions from the following:

5×2=10

a) i) Show that the interplanar distance between two successive planes for a cubic lattice,

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \text{ (Symbols have their usual significance.)}$$

ii) Find out the ratio of spacing of d_{100} , d_{110} and d_{111} fcc lattice planes. 3+2

b) i) Show that if entropy is additive, then thermodynamic probability must be multiplicative.

ii) Under which conditions Boltzmann distribution law may be applicable? 3+2

c) i) State the Lewis-Randall statement of the third law of thermodynamics and justify it from the concept of thermodynamic probability.

ii) Ice has residual entropy—Explain. 3+2

3. Answer any two questions from the following:

10×2=20

a) i) What is a primitive and non-primitive unit cell?

ii) (0,0,0) is the centre of an octahedron. Designate all the faces by Miller indices.

iii) Write down the Bragg's equation for second-order diffraction.

iv) Comment on the validity of Bragg's equation.

v) For first-order reflection from 100 planes with the same radiation, glancing angles for NaCl and KCl were found to be 5.9° and 5.3° , respectively. Find out the ratio of their unit cube edges. (Molar volumes of NaCl and KCl crystals are 37.46 and 27.94 cc) 2+2+1+2+3

b) i) Write down the Boltzmann distribution law in the case of a degenerate system, clearly stating the terms involved.

ii) With the increase of temperature, the number of particles in the higher energy level increases—justify the statement.

iii) A system has three distinguishable particles distributed among three compartments in all possible ways. Calculate the total number of microstates.

iv) Derive the expression for the vibrational partition function for a diatomic molecule.

2+2+3+3

c) i) Heat capacity, $C_v < 3R$ at very low temperature—Explain.

ii) Show that for a polymer, the mass average molar mass (M_w) $\geq$ Number average molar mass (M_N).

iii) Write down the expression for the calculation of the absolute value of entropy when a substance is heated from 0 to T Kelvin temperature ($T > T_b$; T_b is the boiling point)

iv) A hydroxy acid, $\text{HO}-(\text{CH}_2)_5-\text{COOH}$, is polymerized, and it is found that the product has a number average molar mass of 20000 g mol^{-1} . Calculate the degree of polymerization.

3+3+2+2