Unit II

4. (a) Derive an expression for entropy production due to mass flow.

(b) Discuss Electro-Kinetic phenomenon in detail. **8×2=16**

5. (a) Discuss the theory of fluctuations. Derive and expression of fluctuations in density.

(b) State and explain the principle of microscopic reversibility and the Onsager reciprocal relation. **8×2=16**

Unit III

6. Find the commutator relation for the following : **4×4=16**

(i) $\left[\hat{J}_y, \hat{J}_z\right]$

No. of Printed Pages : 06 Roll No. .....

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M.Sc. EXAMINATION, 2025

(Fourth Semester)

(2023-24 Onwards)

(Regular & Re-appear)

CHEMISTRY

Physical Chemistry Special-V

Statistical, Non-equilibrium Thermodynamics and Quantum Mechanics

Time : 3 *Hours*] [*Maximum Marks :* 80

Note : Attempt *Five* questions in all, selecting *one* question from each Unit. Q. No. **1** is compulsory. All questions carry equal marks.

(Compulsory Question)

1. (a) What is a Partition Function ? Write any *two* features of partition function.

(b) Give a comparison of Maxwell-Boltzmann and Bose-Einstein.

(c) Write angular momentum operators L_y, L_z in Cartesian co-ordinate.

(d) What is Onsager's reciprocity relation ?

(e) Find the commutator for $[L_x, L_y]$

(f) Write the postulates of non-equilibrium thermodynamics.

(g) Write the secular determinant for ethylene molecule using Huckel Molicular Orbital theory.

(h) What are Bosons and Fermi particles ?

8×2=16

Unit I

2. (a) Maximizing the thermodynamic probability of a macrostate and involving Langrange's undetermined multiplier, derive the expression for Fermi-Dirac Statistics.

(b) Using Fermi-Dirac Statistics, derive the expression for specific heat of electron gas. **8×2=16**

3. (a) Derive an expression for Bose-Einstein statistics compare it with Fermi-Dirac statistics. State under what conditions the two become equal.

(b) Using Bose-Einstein statistics, derive the expression for the energy of Bosons.

8×2=16

(ii) $\left[L^2, L_z\right]$

(iii) $\left[L^2, L_-\right]$

(iv) $\left[\hat{J}_+, \hat{J}_-\right]$.

7. (a) Derive the expression for total orbital angular momentum and spin angular momentum in Cartesian coordinates.

(b) What are ladder operators ? Explain in detail. **8×2=16**

Unit IV

8. Apply the approximation of Huckel Molecular Orbital Theory for Butadiene and hence give the corresponding energy expression and wave function. **16**

9. Apply the HMO theory to set up and solve Huckel determinant equation for cyclopropenyl radical and its cation and anion. Explain the information obtained in detail. **16**

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