M. Sc. Chemistry Examination, 2022

(4th Semester)

Physical Chemistry Special

Paper – XVI-P

Time : Two hours Full Marks : 50

(25 marks for each unit)

Use a separate answer script for each Unit.

UNIT: P-4161

1. a) Napthalene molecule with the ten p_z-orbitals of carbon atoms as bases may be represented as the sum of irreducible representations A_u, B_{1u}, B_{2g}, and B_{3g} – Justify.

Using projection operator technique construct one symmetry-adapted normalized πMO wave function belonging to A_u symmetry. 4+5

OR

Benzene molecule with the six p_z-orbitals of carbon atoms as bases may be represented as the sum of irreducible representations A, B, E_1 and E_2 – Justify.

Using projection operator technique construct one symmetry-adapted normalized πMO wave function belonging to E_1 symmetry. 4+5

b) Assign the symmetry of the pure normal modes of NH_3 through internal coordinate method. Show which of them are IR and Raman active. 4

2. a) Construct sp^2 hybride orbitals of CO_3^{-2} ion which belong to the D_{3h} point group. 4

Or

Find out which atomic orbitals of the atom A hybridize to form σ bonds with B for a molecule AB_5 belonging to C_{4v} point group. 4

b) Give reasons on the basis of symmetry why thermal and photo-chemical bond breaking of cyclobutene derivatives produce different stereo isomers. 4

c) Show how the degenerate set of five d orbitals of a free metal atom split under an octahedral environment of ligands in a complex. 4

[***Note:*** Character Table for required point groups will be supplied at the time of examination.]

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*Answer **all** the questions.*

3. Consider a free electron gas in three dimensions and hence derive an expression for the electron velocity at the Fermi surface. Comment on the factor(s) that will affect it. 6

4. What is Hall Effect? Deduce the necessary expression(s) to calculate the carrier concentration. 5

5. For alkali halide crystals like NaCl, two values of the activation energy for self-diffusion are observed – explain. 3

6. Assuming the two-sublattice model, derive an expression for the susceptibility of an antiferromagnetic material when $T > T_N$. 5

7. Justify and draw the qualitative energy level diagrams of a metal (M) and a p-type semiconductor (S) contact when $\phi_M > \phi_S$ (ϕ being the work function) before and after equilibrium has been established. What would be the nature of such a contact? $3\frac{1}{2}$

8. Write a short note on (any ***one***): $2\frac{1}{2}$

i) Piezoelectric effect

ii) dc Josephson effect