M. Sc. Chemistry Examination, 2018

(4th Semester)

Physical Chemistry Special

Paper - XVI-P

Time : Two hours Full Marks : 50

(25 Marks for each Unit)

Use a separate answerscript for each unit.

UNIT – P- 4161

1. a) (i) Naphthalene molecule with the ten p_z -orbitals of carbon atoms as bases may be represented as the sum of irreducible representations A_u, B_{lu}, B_{2g} and B_{3g} –Justify. 4

(ii) Using projection operator technique construct one symmetry-adapted normalized πMO wave function belonging to A_u symmetry. 5

b) Assign the symmetries of the genuine normal modes of H_2O. Which of these modes are IR and Raman active ? 3

2. a) Construct sp^2 hybrid orbitals of CO_3^{-2} ion which belongs to the D_{3h} point group. 5

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.

b) In the chemical reaction cyclobutene $\leftrightarrow$ cis-butadiene, show how the symmetry orbitals of the reactant and the product correlate under the disrotatory mode of conversion. 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.]

UNIT – P- 4162

3. a) Consider a free electron gas in three dimension and hence find out an expression for the electron velocity at the Fermi surface and comment on which factor it depends. 6

Or

The thermal conductivity of a Fermi gas is directly proportional to the temperature – Prove.

b) What is Hall effect ? Deduce an expression for the Hall coefficient and explain its significance. 5

c) The alkali halide crystals like NaCl or KCl are colorless in their pure form, but when heated in the vapor of the corresponding metal they bocome colored .– Justify. 2

4. a) Derive the condition for systematically absent (hkl) reflections for a bcc lattice and hence show which of the reflections among (110), (200), (210), (121), (220) and (212) will be observed and which will not in the X-ray diffraction pattern of such a crystalline material. 5

b) Assuming the two-sublattice model, express the Nèel temperature (T_N) in terms of β and α, the interaction parameters for two unlike atoms and two like atoms, respectively. How is T_N related with θ ? 4

Or

Draw qualitative energy level diagram of the junction made of two dissimilar metals at equilibrium explaining all the terms involved in it. What changes take place when such a junction is biased with an external voltage and state whether the junction can, in principle, be used as a rectifier.

c) Write a short note on ***(any one)*** : 3

i) BCS theory of superconductivity

ii) Piezoelectric effect