M. Sc. Chemistry Examination, 2019

(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. Answer *any one* :

   a) (i) Matrices, which describe the transformations of a set of k eigenfunctions corresponding to a k-fold degenerate eigenvalue, form a k-dimensional representation of the group – Justify.

   (ii) The functions ψ_1 and ψ_2 transform according to the irreducible representation A_1, and E, respectively, while the operator $\widehat{M}$ corresponding to an observable transforms according to A_2 representation of the point group C_{3v}. Check with justification whether the integral $\langle \psi_1 | \widehat{M} | \psi_2 \rangle$ vanishes or not.

                                                        2+2

Or

[Turn over

b) Using the Great Orthogonality theorem, construct the symmetry projection operator for i-th irreducible representation. 4

2. Answer *any three* of the following : 7×3

a) Apply the method of inspection to construct the $d^2 sp^3$ hybrid orbitals of a AB_6 molecule belonging to O_h point group.

Or

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

b) Write down the Woodward-Hoffmann rule. In the electrocyclic reaction of *cis*-1,3-butadiene to cyclobutene, show how symmetry oribtals of the reactant correlate with those of the product under the conrotatory mode of conversion.

Or

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

c) Show how one can assign the symmetry types of the genuine normal modes of BF_3, which belongs to D_{3h} group. Which of these modes are IR and Raman active ?

b) When do you expect a rectifying behavior for the junction of a metal (M of work function ϕ_M) and an n-type semiconductor (S of work function ϕ_S) ? Explain your answer with the necessary energy level diagrams at equilibrium and under variously biased conditions. 5

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

i) F-centre

ii) Ferroelectric effect

iii) First Brillouin zone

UNIT – P- 4162

Answer *all* the questions

3. a) Derive a quantitative expression for the electronic heat capacity of the free electron gas valid at low temperatures $T \ll T_F$ (Fermi temperature) and hence show that it varies linearly with the temperature. $5\frac{1}{2}$

    b) Obtain an estimate of the stabilization energy of the superconducting state with respect to the normal state at absolute zero. 4

    c) For normal ferromagnetic behavior, the expected saturation magnetic moment per Fe_3O_4 molecule is 14 Bohr Magneton (BM), whereas the experimentally observed value is 4·08 BM – Explain. $3\frac{1}{2}$

    #### Or

    Show that the reciprocal lattice to an fcc lattice is a bcc lattice.

4. a) Derive an expression for the structure factor for a I-lattice and explain which of the (hkl) reflections among (100), (110), (111), (200), (210), (211), (220) will be absent in the diffraction pattern of such a crystalline solid. 4

Or

Find the symmetries of the genuine normal modes of linear HCN molecule using integration method. Show which of them are IR and Raman active.

d) For a d^2 system in octahedral chemical environment, how many states are possible when the crystal field strength is very large relative to inter d-electron correlation ? Show how these states correlate with the Terms arising out of the weak field interaction.

Or

Using Huckel approximation, evaluate the energies corresponding to SALCs after constructing them for cis-butadiene. Calculate the delocalization energy of the molecule.

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