M. Sc. (Chemistry) Examination, 2023

(4th Semester)

Paper: XVI–P

[Physical Chemistry Special]

Time : Two Hours Full Marks : 40

(20 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} and B_{3g} — Justify using projection operator technique and 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 and construct one symmetry-adapted normalized πMO wave function belonging to E_1 symmetry. 4+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 belong 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. 5

b) Give reasons on the basis of symmetry why thermal and photo-chemical bond breaking of cyclobutene derivatives produce different stereo isomers. 3

Unit: P-4162

Answer ***all*** the questions.

3. Derive a quantitative expression for the electronic heat capacity of the free electron gas valid at low temperatures $T<<T_F$ (Fermi temperature) and hence show that it varies linearly with the temperature. 6

4. Show that the scattering amplitude of X-rays becomes a maximum when the change in wave vector of the scattered X-rays $\left(\Delta\vec{k}\right)$ becomes equal to a reciprocal lattice vector $\left(\vec{G}\right)$ of the crystal. 5

Or

Express the structure factor in terms of atomic form factor for an fcc lattice and hence explain why reflections

from the (211) planes vanish, but those from (111) planes appear strongly in the X-ray diffraction pattern corresponding to such a lattice. 5

5. The expected saturation magnetic moment per Fe_3O_4 molecule is 14 Bohr Magneton (BM) assuming it to show normal ferromagnetic behaviour, but the experimentally observed value is 4.08 BM – Explain on the basis of two sub-lattice models. 5

Or

Justify and draw the qualitative energy level diagram of a metal (M) and an n-type semiconductor (S) contact at equilibrium (assume $\phi_M > \phi_S$; $\phi =$ work function). Derive an expression for the thickness of the barrier layer formed at such a junction. 2+3

6. Obtain an estimate of the stabilization energy of the superconducting state with respect to the normal state. 4

Or

Write a note on piezoelectricity. 4