

M.Sc. Examination, 2019
Semester-IV
Chemistry
Course: CH-1019 (Elective)
(Physical Chemistry)

Time: Three Hours

Full Marks: 40

Questions are of value as indicated in the margin.

Answer **any four** questions.

1. a) What is Franck-Condon integral and what is its significance? 2
 b) State the Teller's non crossing rule regarding potential energy surface. 1
 c) Discuss environmental effect on absorption and emission spectra. Show how solvent perturbation technique can be used to identify $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition. 3+1
 d) Describe the fluorescence spectroscopic method for determination of pK^* of a photoacid. 3
2. a) Write down the unimolecular photophysical processes that can occur in a molecule. Also indicate their approximate time scale of occurring. 2
 b) Relative fluorescence quantum yield of quinoline in benzene, ethanol and water are 1:30:1000 – explain why? 1
 c) What is fluorescence excitation spectra? Show that fluorescence excitation spectra reproduce the absorption spectra of a molecule. 1+2
 d) Considering the photophysical kinetics of a molecule, derive the following relation:

$$\frac{\phi_p}{\phi_f} = \frac{k_{ISC}}{k_f} \left(\frac{k_p}{k_{ISC}^T + k_p} \right).$$
 4
3. a) What is Flory-Huggins polymer-solvent interaction parameter? How this parameter depends on temperature? 2+1
 b) Show that molar mass of the solute can be determined by excess Rayleigh ratio (ΔR). 4
 c) How molar mass average of polymer are determined from $[W(M)]$ weight fraction molar mass distribution. 3
4. a) Derive the Clausius-Mosottii equation:

$$\frac{\left(\frac{\epsilon}{\epsilon_0} \right) - 1}{\left(\frac{\epsilon}{\epsilon_0} \right) + 2} \frac{M}{\rho} = \frac{1}{3 \epsilon_0} N_A \alpha_d.$$
 4
 b) Establish the relation between paramagnetic susceptibility and molar magnetic susceptibility. From this relation compute the number of unpaired electron in a molecule of a substance. 3
 c) Explain qualitatively why at very high temperature molar polarization of HCl, HBr and HI follow this order $P_m(HCl) > P_m(HBr) > P_m(HI)$. 3
5. a) What do you mean by primitive vector of a lattice? With reference to a 2D oblique lattice show that choice of primitive vector is not unique. 3
 b) Describe the crystal structure of ZnS. Show that each Zn atom in that is surrounded by four S atoms in a tetrahedral orientation. 4
 c) What do you mean by closed packing structure? How many ways are there for such kind of packing? Distinguish between FCC and hcp structure. 3

P.T.O.

6. a) What is reciprocal lattice? Prove that reciprocal lattice is also a Bravais lattice. 3
- b) For a BCC lattice, a plane is defined by Miller indices $\{1\ 1\ 1\}$. Construct the corresponding reciprocal vector and hence calculate the interplanar distance. 3
- c) Consider a 2D lattice defined by primitive vectors a_1 and a_2 of equal length but aligned with an angle of 60° . First, construct Wigner Seitz cell and then first Brillouin zone of that lattice and mark the high symmetry points. Comment on the orientation of those cells. 4
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