

Five Year Integrated M.Sc. Examination, 2017

Semester - VI

Course: CH-3-6-4

(Chemistry: Spectral Methods-II)

Time: Three Hours

Full Marks: 40

Questions are of value as indicated in the margin.

Answer **Question No.1** and **any three** from the rest.

1. Answer **any five** questions: 5x2=10
 - a) Calculate the energy of an Einstein associated with a wavelength of 275 nm.
 - b) What is the full form of "ESCA"? Write its basic principle.
 - c) A ground state ^{57}Fe nucleus placed in the path of γ -rays, emitted by an excited ^{57}Fe nucleus, is unable to re-absorb. Why?
 - d) What do you mean by XAFS? What information do we gather from it?
 - e) What are the photosensitized reactions? Discuss with suitable example.
 - f) What is excimer emission?
2.
 - a) Draw a schematic diagram of a Mössbauer spectrophotometer. A multi-channel computer is necessary to record the γ -rays spectroscopy. Why? 3
 - b) The Mössbauer spectrum of $[\text{Fe}(\text{CN})_6]^{4-}$ shows a single line, whereas, $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ shows a doublet. Explain with suitable energy diagram. 4
 - c) In case of heterocyclic compounds, phosphorescence appears at low temperature. Why? 3
3.
 - a) What is chemical shift or isomer shift in Mössbauer spectroscopy? Which factor(s) govern the magnitude as well as sign of the isomer shift? 1+2
 - b) The Mössbauer spectrum of iron difluoride, FeF_2 , shows asymmetrically spaced six lines. Explain with suitable energy diagram. 4
 - c) Pyridine, which is isoelectronic N-analogue of benzene, is non-fluorescent in non-polar solvent, but fluorescent in polar solvent. Why? 3
4.
 - a) What are the radiative and non-radiative processes in photochemistry? Discuss with the help of Jablonski diagram. 3
 - b) Derive the expression of the quantum yield of phosphorescence (ϕ_p) from the Jablonski diagram drawn in 4(a). 4
 - c) The photodecomposition of HI vapour is carried out with $\lambda = 2070 \text{ \AA}$ radiation. Absorption of each calorie gives $1.44 \times 10^{-5} \text{ gm}$ of hydrogen. What is the quantum yield? 3
5.
 - a) Discuss the methods that can be used to increase the intensity of phosphorescence emission. 3
 - b) State the law of "Stark and Einstein". Absorbance of a solution containing compounds A and B at wavelengths 310 and 370 nm are 0.45 and 0.25, respectively. Calculate the concentrations of A and B from the following data. $\epsilon_A(310 \text{ nm}) = 1.2 \times 10^4 \text{ L mol}^{-1}\text{cm}^{-1}$, $\epsilon_A(370 \text{ nm}) = 0.25 \times 10^4 \text{ L mol}^{-1}\text{cm}^{-1}$, $\epsilon_B(310 \text{ nm}) = 0.2 \times 10^4 \text{ L mol}^{-1}\text{cm}^{-1}$, $\epsilon_B(370 \text{ nm}) = 2.5 \times 10^4 \text{ L mol}^{-1}\text{cm}^{-1}$. 1+3
 - c) What are the basic differences between Ultra-Violet photoelectron spectroscopy and X-ray photoelectron spectroscopy? What is Auger Electron Spectroscopy (AES)? What is its application? 3
6. Write short notes on: 2x5
 - a) "P-type delayed fluorescence",
 - b) "Fluorescence and structure"