

9. (a) Apply HMO theory to the π -electron system of ethylene to arrive at the energy levels and the wave functions.

Or

- (b) Determine the hybridization scheme of sigma bonding in methane molecule, applying quantum mechanism.

10. (a) (i) Draw and explain the $^1\text{H-NMR}$ spectrum of acidified ethanol. (5)
- (ii) What is chemical shift? How is it affected by various factors? (5)

Or

- (b) Explain the theory, selection rules and applications of ESR spectroscopy. (10)
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S.No. 416

08PCH08

(For the candidates admitted from 2008 – 2009 onwards)

M.Sc. DEGREE EXAMINATION, APRIL/MAY 2018.

Third Semester

Chemistry

PHYSICAL CHEMISTRY - III

Time : Three hours

Maximum : 75 marks

PART A — (5 × 5 = 25 marks)

Answer ALL questions.

1. (a) Deduce the relation $\ln X! = X \ln X - X$ for large values of X.

Or

- (b) What is an ensemble? Explain its types.
2. (a) State and explain the principle of microscopic reversibility.

Or

- (b) What are phenomenological equations? Give their significance.

3. (a) What is flash photolysis? Explain its salient features.

Or

- (b) Describe the kinetics of a consecutive reaction.

4. (a) Write the trial wave function for H_2^+ and H_2 molecule. In H_2 molecule, point out which one are ionic and which one are covalent.

Or

- (b) Describe the Hartree-Fock self consistent field method to explain the total energy of various atomic orbitals.

5. (a) Narrate the theory and conditions of NMR.

Or

- (b) What is 'g' value? How is it affected by various factors? Explain.

PART B — (5 × 10 = 50 marks)

Answer ALL questions.

6. (a) Prove that complete partition function for a system is the product of translational, rotational, vibrational and electronic partition functions.

Or

- (b) Derive the Maxwell-Boltzmann distribution law. Mention its uses.

7. (a) Derive the Onsager's reciprocal relations. Mention its significance.

Or

- (b) Derive an expression of entropy production arising from heat interaction between two systems.

8. (a) Explain the mechanism of H_2-Br_2 photochemical reaction and derive the rate law for this reaction.

Or

- (b) Describe the three explosion limits that occur in hydrogen-oxygen system. Mention the reasons for the existence for the limits.