(For the candidates admitted from 2012–2013 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) What are micro states and macro states? Calculate the number of micro states for a system in which four particles are distributed in five energy levels.

Or

(b) Write the expression for rotational partition function. Calculate the rotational partition function of HCl at 300 K the moment of inertia of HCl is 2.66×10^{-40} g/cm^2.

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9. (a) Write the important postulates of Huckel molecule orbital theory and apply the same to butadiene system.

Or

(b) (i) Write the slater's rule, calculate the effective nuclear charge of a valence electron of fluorine atom.   (4)

(ii) Write an account on self consistent filed theory.   (6)

10. (a) Discuss the theory of NMR spectroscopy.

Or

(b) (i) What is spin - spin coupling? Explain it by giving suitable examples.   (5)

(ii) What is Mc Connel relationship? Write its importance.   (5)

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2. (a) What is entropy production? How is it related with flux? Explain.

Or

(b) Write an account on Onsager's reciprocal relation.

3. (a) What are consecutive and parallel reactions? Explain them by giving suitable examples.

Or

(b) Write an account on explosion limits.

4. (a) State Born-Oppenheimer approximation Why is it introduced? Write the Hamiltonian using this approximation and State under what condition this approximation is valid.

Or

(b) Construct SP hybrid orbitals by combining one 2s and one 2p atomic orbitals and write the wave function for the same.

5. (a) What is chemical shift? How is it expressed? Describe the factors affecting the chemical shift.

Or

(b) What is the source of energy to record ESR spectrum? Write the selection rule for a nucleus to be ESR active. Define g - value in ESR write the 'g' value for a free electron.

PART B — (5 × 10 = 50 marks)

Answer ALL questions.

6. (a) Give a comparative account of Maxwell - Boltzmann, Fermi-Directive and Bose Einstein statistics.

Or

(b) Compare the Einstein and Debye approaches to the heat capacity of solids.

7. (a) Write an account on stationary non equilibrium state.

Or

(b) Write the entropy production, Phenomenological equations for the electro kinetic process. obtain separate Onsager reciprocal equations for electro kinetic phenomena, from the equations arrive Saxen's equations.

8. (a) What are fast reactions? Discuss how the kinetics of fast reactions are studied by relaxation methods.

Or

(b) Discuss the general treatment of chain reactions.