**ST. JOSEPH’S COLLEGE(AUTONOMOUS), BANGALORE-27**

**II SEMESTER EXAMINATION, APRIL 2017**

**M.Sc., CHEMISTRY**

**CH- 8315: Physical Chemistry**

**Time 2 ½ hours** **Max.Marks: 70**

**This question paper has THREE parts A, B and C and two printed pages.**

**PART- A**

**Answer any SIX of the following: 6 x 2 = 12 marks**

1. What is partition function and give the expression for it.
2. Give the conditions for the formation of kinetic and thermodynamic products.
3. What is flash photolysis?
4. Define partial molal free energy.
5. What are thermodynamic excess functions?
6. Explain the electrokinetic phenomena.
7. What is meant by ensemble averaging?
8. Write the Sackur-Tetrode equation.

**PART- B**

**Answer any FOUR of the following: 4 x 12 = 12 marks**

1. (a) Derive an expression for the influence of solvent dielectric constant on the rates of reaction between ions using double sphere model.

(b) Discuss the Hinshelwood theory of unimolecular reactions and mention its limitations. (7+5)

1. (a) Give the Rice and Herzfeld mechanism of pyrolysis of acetaldehyde and derive the expression for the rate of formation of methane.

(b) Compare between RRK and RRKM theories with suitable mechanisms. (7+5)

1. (a) Discuss the free radical mechanism of co- polymerization.

(b) For a microscopic reversible system show that the Onsagar reciprocity relation

L12 = L21 (5+7)

1. (a) Derive the expression for the rate constant of a bimolecular reaction in terms of partition functions using transition state theory.

(b) Derive the expression for (i) free energy of mixing and (ii) entropy of mixing for a pair of non-ideal gases. (6+6)

1. (a) Derive expression for vibrational partition function keeping zero point energy as the reference.

(b) Derive Bose –Einstein statistics. (4+8)

1. (a) Derive equipartition principle from the concept of partition function.

(b) Outline the determination of partial molal volume by apparent molal method?

(c) How are the fast reactions studied by NMR technique? Explain. (4+4+4)

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**PART- C**

**Answer any TWO of the following: 2 x 5 = 10 marks**

1. a) Calculate the rotational partition function for NH3 at 25⁰C. The three moments of inertia are 2.78 x 10-47; 2.78 x 10-47and 4.33 x 10-47kg m2 respectively. Given that, σ for NH3 = 3.

b) Calculate the value of ln 8! with and without using Stirling’s approximation. (3 +2)

1. For a van der Waals gas, express the fugacity as a function of V, T, R and van der Waals constants.
2. Calculate the excess volume when sufficient ethanol is added to water to get one litre of solution with composition of mole fraction of ethanol = 0.6. Partial molal volume of ethanol and water are 57.0 and 17.0 cm3mol-1 respectively at the given composition.

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