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DATE: **13** **-04-2018 (1 PM)**

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

M.Sc CHEMISTRY – II SEMESTER

SEMESTER EXAMINATION, APRIL 2018

CH-8315- Physical Chemistry

Time: 2½ hours Max.Marks: 70

(For supplementary candidates of 2014 batch only)

Do not write the register number on the question paper

Please attach the question paper along with the answer script.

This question paper contains two pages and three parts.

PART-A

Answer any six of the following questions. 6 x 2 =12 marks

1. Define partial molal entropy. What is its significance?
2. What are the criteria for thermodynamic standard state of liquid and gas?
3. What is Boltzmann factor? How does it become useful in statistical thermodynamics?
4. Define the term flux. What is the driving force for the heat flux?
5. Define the term electroosmosis.
6. Write the expression for the total number of collisions between molecules of A and molecules of B and explain terms in it.
7. Distinguish between the Lindemann theory and Hinshelwood theory of unimolecular reactions?
8. What are the limitations of collision theory?

PART-B

Answer any FOUR of the following questions. 4 x 12 = 48 marks

1. (a) Define apparent molal volume. How is this method employed in the determination of partial molal volume of salt-water systems?

(b) Derive the expression for the entropy of mixing of non-ideal gases.

(c ) Obtain the expression for the fugacity of a real gas in terms of pressure. (4+4+4)

1. (a Derive the expression for the rotational partition function.

(b) Calculate the translational contribution to the entropy of monatomic gas in terms of atomic weight.

(c) The vibrational frequency of iodine is found to be 208 cm-1. At what temperature will the population of the first excited state is half of the ground state? (4+4+4)

1. (a) Derive Maxwell-Boltzmann statistics for the molecules present in a system of non-degenerate energy levels.

(b) State the postulates of statistical thermodynamics and explain. (8+4)

1. (a) Discuss diffusion controlled reactions.

(b) Draw the potential energy diagram for the addition of 1 equivalent of HBr to 1,3-butadiene and indicate kinetic and thermodynamic products.

(c) Discuss the kinetics of cationic polymerization. (4+3+5)

1. (a) How do you study the kinetics of fast reactions by continuous and stopped flow techniques?

(b) Write the hydrogen-oxygen chain reaction mechanism and discuss the effect of pressure on this reaction. (6+6)

1. (a) Discuss the entropy production due to the chemical reaction.

(b) Discuss the RRK theory of unimolecular reactions. (6+6) CH-8312-A-18

-2-

PART-C

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

1. At 298K density of 45% by mass of ethanol in water is 0.92 gcm-3. The partial molal volume of water at the above composition is 17.4 cm3mol-1. Calculate the partial molal volume of ethanol and volume of mixing. (Density of ethanol and water 0.78 and 0.97 gcm-3 respectively).
2. 24.0 g of non-volatile solute of molecular weight 241.0 g mol-1 has ∆Tf of 0.359°C. Calculate the activity coefficient (Kf = 0.52Kkgmol-1).
3. Draw schematic plots indicating the variation of log (k/k0) with the square root of ionic strength on the rates of the following reactions:

(i) [Co(NH3)5Br]2+ + Hg2+ + H2O → [Co(NH3)5H2O)]3+ + HgBr+

(ii) BrCH₂COO⁻ + S₂O₃²⁻ → ⁻S₂O₃CH₃COO⁻ + Br⁻

(iii) [Co(NH₃)₅Cl]²⁺ + OH⁻ → [Co(NH₃)₅OH]²⁺ + Cl⁻

(iv) (C₂H₅)₃N + C₂H₅I → (C₂H₅)₄N⁺ I⁻

(v) [Cr(H2O)6]3+ + CNS- → [Cr(H2O)5CNS]2+ + H2O

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