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Register Number:

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

**M.Sc CHEMISTRY – II SEMESTER**

**SEMESTER EXAMINATION, APRIL 2017**

**CH-8315- Physical Chemistry**

**Time: 2 ½ hours Max.Marks: 70**

This question paper contains two pages and three parts.

PART-A

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

1. Obtain the expression for variation of activity with pressure at constant temperature.
2. Derive Henry’s law from the concept of chemical potential.
3. Write the expression for the total partition function for a system of N particles when they are (i)distinguishable and (ii) indistinguishable.
4. Define (i) Flux and (ii) Microscopic reversibility.
5. Give the expression for the rate constant of a diffusion controlled reaction between two reactant molecules A and B.
6. Mention the limitations of Lindemann's theory of unimolecular reactions.
7. From the following figure identify and write the structures of the kinetic and thermodynamic products (SM: starting Material, TS's: transition states and P1 and P2 :products).



1. Give the phenomenological laws of transport processes and explain the terms.

PART-B

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

1. (a) Derive Gibbs Duhem equation.

(b) Obtain the relation between the activity coefficient of solvent and solute in a binary solution.

(c) Calculate the composition of a binary mixture for which the entropy of mixing is maximum.

 (4+4+4)

1. (a) Deduce Konovolov laws from the Gibbs Duhem Margules equation.

(b) Derive the expression for the translational partition function. (6+6)

**CH-8315-B-17**

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1. (a) Obtain the relationship between thermodynamic probability and statistical entropy.

(b) Calculate the proportion of Iodine molecules in their ground, first and second excited vibrational states at 250C (Vibrational wave number is 214.6 cm-1 and iodine vibrations are simple harmonic; kT/hc = 207.23 cm-1) (6+6)

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

(b) Explain the kinetics of chain reactions between hydrogen and oxygen molecules. (7+5)

1. (a) Derive an expression for the entropy production due to flow of mass through a semi permeable membrane.

(b) Discuss the effect of primary salt in ionic reactions. (7+5)

1. (a) Mention the limitations of flow techniques. Explain the flash photolysis for studying the kinetics of fast reactions.

(b) Discuss the RRKM theory of unimolecular reactions. (5+7)

PART-C

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

1. The partial molal volumes of acetone and chloroform in a mixture in which the mole fraction of chloroform is 0.46 are 74.16 and 80.24 cm3/mole respectively. What is the volume of a solution of mass 1.00 Kg.
2. Evaluate the rotational partition function of HCl at 250C for which B = 10.6 cm-1. Compare the populations of first 5 levels. ( kT/hc = 207.23 cm-1)
3. For a particular reaction the rate constant was found to be 2.3 x 10⁻³mol⁻¹dm³s⁻¹ at 50°C. Calculate the free energy change of activation and entropy change of activation for the formation of an activated complex.

Given: h= 6.626 x 10⁻³⁴Js; R = 8.314 JK⁻¹mol⁻¹; N= 6.026 x 10²³ ; ΔH\* = 120.5 kJmol⁻¹.

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