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

**M.Sc CHEMISTRY – II SEMESTER**

**SEMESTER EXAMINATION, APRIL 2017**

**CH 8312 - Physical Chemistry**

**Time: 3 hours Max.Marks: 100**

**(*For supplementary candidates of 2014 and earlier batches)***

***Attach this question paper with the answer script***

This question paper contains three -pages and three parts.

 Constants: kB = 1.3806 x 10-23 JK-1; Є₀ = 8.854 x 10-12C2N-1m-2; e = 1.602 x 10-19 C;

 R = 8.314 JK-1mol-1 ; 1J = kgm2s-2; N=6.023x1023; h=6.626x10-34Js

**PART-A**

**Answer any TEN of the following questions. 10 x 2 = 20 marks**

1. Distinguish between gas phase reactions and reactions occurring in solution.
2. Mention any two drawbacks of the Hinshelwood theory of unimolecular reactions.
3. What are fermions and bosons?
4. Give the general scheme for the kinetics of anionic polymerization.
5. Mention the limitations of collision theory.
6. Mention the conditions required for a reaction to be a) thermodynamically and b) kinetically controlled.
7. Define partial molal entropy. Write its significance.
8. For non-ideal liquid mixtures give the expressions for ∆Gmix and ∆Smix.
9. State Konovalov’s first law What are the differences between Maxwell-Boltzmann and Fermi-Dirac statistics?
10. Write the expressions for molecular and molar partition functions for distinguishable particles.
11. The first excited state 2P1/2 of Chlorine atom lies 0.11 eV above ground state 2P3/2. Calculate the partition function qe. at 1000 K.

**PART-B**

 **Answer any FIVE of the following questions. 5 x 12 = 60 marks**

1. (a) Discuss the flow techniques for studying fast reactions.

(b) Derive an expression for the production of entropy when there is heat interaction between systems A and B and with the surroundings. (6+6)

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

(b) Using the transition state theory derive the expression for the rate constant in terms of partition functions. (6+6)

1. (a) Propose the mechanism for the thermal decomposition of acetaldehyde according to Rice and Herzfeld. Based on this mechanism derive the rate expression for the formation of methane.

(b) Prove that $\left|L\_{ij}\right| \leq \sqrt{L\_{jj}L\_{ii}}$ (6+6)

CH-8312-A-17

1. (a)Starting with Gibbs-Duhem equation derive Henry’s law

(b) How do you determine the fugacity of a real gas by graphical method? (6+6)

1. (a) Define “ Thermodynamic activity” of a substance. Explain the principle, procedure and calculations involved in the determination of activity of HCl in aqueous solutions.

b) Derive ΔGmix=RT Σxi ln xi for an ideal binary mixture. From this relationship obtain an equation for ΔS mix  of a binary mixture. (6+6)

1. (a) Derive an expression for the free energy of a monoatomic gas in terms of T, P and M

(b) CO2 spectrum indicates the following absorptions: 667.4 ,667.4,1388 and 2349 cm-1. Calculate the resultant vibrational partition function at 1000 K by neglecting the contribution of zero point energy.

(c) What is micro canonical ensemble? Represent it by a suitable diagram. (5+4+3)

1. (a) Starting from the concept of partition function obtain the principle of equipartition. Under what conditions it is valid?

(b)Calculate the translational contribution to standard enthalpy, standard entropy, and standard free energy of oxygen molecule. (6+6)

**PART-C**

**Answer any FOUR of the following questions 4 x 5 = 20 marks**

1. Consider the following reaction carried out in water-alcohol mixtures of different compositions at 25⁰C.

$$A^{-2} + B^{-1} ⇋ [A………B]^{-3} ⟶ products$$

Rate constants, are measured at each composition of water-alcohol mixture. A plot of log k vs. 1/Єs (Єs is the dielectric constant of water-alcohol mixtures at various compositions) was found to be linear with the slope equal to – 393.3. Calculate the inter nuclear distance dAB of the transition state.

1. (a) Calculate the diffusion controlled rate constant for the combination of molecules A and B in water at 25⁰C. The coefficient of viscosity of water at 25⁰C is 0.001 Kgm-1 s-1. Express the rate constant value in dm3mole-1s-1.

(b)The Gibbs free energy of a system is given by the relation:G=2.1+1.5Pn1+ 3n2 - n1n2T. Calculate the partial molar volume and entropy at 300K and 101.3 kNm-2. (2.5+2.5)

1. (a) Consider the following Lindemann mechanism for the unimolecular decomposition of a molecule A in the presence of another molecule M

$$A + A \begin{matrix}k\_{1}\\⇌\\k\_{-1}\end{matrix} A^{\*} + A $$

$$A + M \begin{matrix}k\_{2}\\⇌\\k\_{-2}\end{matrix} A^{\*} + M$$

$$A^{\*} → P$$

Derive the rate law for the formation of the product.

(b) Consider the following reaction

 

Identify X and Y and indicate which product is kinetically controlled and which product is thermodynamically controlled. (3+2)

1. (a) A corrupt barman attempts to prepare 100.0 cm3 of a drink by mixing 30.0 cm3 of ethanol and 70.0 cm3 of water at 250 C. Will he get 100.0 cm3 after mixing? Justify and calculate the volumes of water and ethanol that make up to 1000 cm3. (densities of water and ethanol at 250C are 0.997 ,0.80g cm-3, partial malor volumes of them are 18.0 and 53.6 cm3mole-1 respectively.

(b)Under what conditions the partial molar volume of a binary mixture has the following values: (i) 0 (ii) <0 (iii) >0 (3+2)

1. In a rotational spectrum of HBr the maximum intensity was observed for J=4 to J=5 transition at spacings of 16.92 cm-1. Calculate the temperature of the experiment.