ST. JOSEPH'S COLLEGE - AUTONOMOUS, BENGALURU-27
SEMESTER EXAMINATION; APRIL-2022
(to be conducted in July-2022)
M. Sc. Chemistry – II Semester
CH/OCH-8321- PHYSICAL CHEMISTRY

Time: 2½ Hours   **Max. Marks: 70**

Note: This question paper has THREE parts and SEVENTEEN questions. Physical constants
$h = 6.626 \times 10^{-34}$ J s, $k_b = 1.38 \times 10^{-23}$ J K^{-1}, $c = 3 \times 10^8$ m s^{-1} $P^0 = 101235$ N m^{-1}

Part A

Answer any SIX of the following questions: **[2 x 6 = 12]**

1. Evaluate the diffusion-controlled rate constant for the reaction between two molecules (having identical radii) in n-hexane at 298 K. The viscosity coefficient of n-hexane at this temperature is 3.25×10^{-4} kg m^{-1} s^{-1}.

2. Discuss the role of water in the polymerization of isobutene catalyzed by BF_3.

3. State and explain the second postulate of irreversible thermodynamics.

4. Explain the principle of flash photolysis.

5. Why statistical methods are employed in calculation of thermodynamic properties?

6. Represent the microcanonical ensemble by a suitable diagram.

7. Derive an expression for variation of chemical potential with pressure at constant temperature.

8. Write an expression relating activity coefficient of solute and solvent in a dilute solution. Explain the terms involved.

Part-B

Answer any FOUR of the following questions: **[12 x 4 = 48]**

9. a) Discuss the kinetics of decomposition of acetaldehyde and prove that it follows three halves kinetics consistent with the mechanism proposed by Rice and Herzfeld.

   b) Write appropriate mechanism for chain reaction and applying steady state model, derive an expression for the overall formation of the product. Discuss the condition for explosion and explosion limit.   (6+6)

10. a) Derive an expression for the entropy production and its rate in mass flow.

   b) A second order reaction in solution has rate constant 2.34×10^{-2} dm^3 mol^{-1} s^{-1} at 400 ^{0}C. The activation energy is 150 kJ mol^{-1}. Calculate $\Delta^{\#}G^0$, $\Delta^{\#}H^0$, $\Delta^{\#}S^0$ and the pre-exponential factor for the reaction.   (7+5)

11. a) Derive thermodynamic formulation of conventional transition state theory and obtain an expression for the rate constant of a unimolecular reaction.

b) Write free radical mechanism, apply steady state to explain the kinetics of polymerization and prove that the overall order of the reaction is 2. (6+6)

12. a) Derive an expression for translational partition function.

b) At 25 ^{0}C the density of 40% by mass of acetone in water has a density of 0.950 g cm^{-3}. Calculate partial molal volume of acetone if the corresponding value for water under same conditions is 17.3 cm^{-3} mole.

c) Calculate the limiting values of rotational contribution to the standard free energy and standard entropy of hydrogen chloride. (B=10.6 cm^{-1}) (4+4+4)

13 a) Derive Gibbs-Duhem equation. Write its significance.

b) Starting from the concept of chemical potential obtain an expression for Raoult's law.

c) A container at 300 K is partitioned in to two parts. One part contains 1.0 mole of hydrogen at 3.0 atm and the other contains 3.0 mole of nitrogen at 1.0 atm pressure. Calculate the free energy and entropy of mixing. (4+4+4)

14. a) Arrive at the principle of equipartition of energy using the partition coefficient.

b) Explain the principle procedure and calculations involved in the determination of activity. coefficient of H$^+$ in dilute solution of Hydrochloric acid.

c) State the assumptions of Maxwell–Boltzmann statistics. (4+5+3)

Part-C

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

15 a) Calculate the total number of energy levels available for molecules of hydrogen at 300 K.
b) Why is it impossible to measure absolute values of entropy of a system. (3+2)

16. a) Discuss the effect of solvation on the reaction rate for the following reactions if 1,4-dioxane solvent is used.

 + CH$_3$Cl → [??]$^{\#}$ → Products
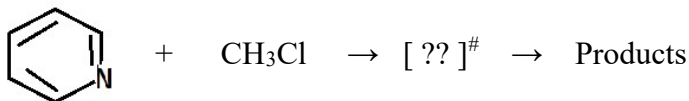
b) The activation energy for the hydrolysis of aspirin at 345 K is found to be 15.0 kJ mol^{-1}. If there were one million collisions, how many molecules have sufficient energy to react and form the product? (3+2)

17. The dielectric constants of some solvents are as follows: methanol=33, ethanol=25, DMF=37, acetone=21, and DMSO=49. Answer the following questions:
a) in which one of these solvents the reaction rate between a pair of ions is highest?
b) Arrange the solvents in the increasing order of reaction rate between a pair of ions and explain the order of the arrangement.
c) What's the effect of increasing the charge number on reaction rate?