LOYOLA COLLEGE (AUTONOMOUS) CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – **CHEMISTRY**

THIRD SEMESTER – **APRIL 2025**

PCH 3502 – THERMODYNAMICS AND CHEMICAL KINETICS

Date: 26-04-2025 Dept. No. Max. : 100 Marks

Time: 09:00 AM - 12:00 PM

SECTION A

Answer any FOUR questions. **(4 × 10 = 40)**

1. Derive Gibbs-Duhem equation. Mention its significances.
2. a) Draw and explain the phase diagram of a ternary system consisting of two solids and water with the formation of a double salt.
   b) The fugacity coefficient of a gas at 300 K and 25 atm is 0.92. Calculate the difference in chemical potential of the real gas and an ideal gas. (7+3)
3. Predict the condition for internal entropy production to maintain thermal equilibrium.
4. a) Obtain an expression to show the relationship between partition function and entropy.
   b) Write the phenomenological equations for electro kinetic effects and deduce their cross coefficients. (6+4)
5. a) Discuss the construction of potential energy surface with an example and mention its significance.
   b) For a second order reaction, the rate constant at 298 K is 4.0×10^{-6} $M^{-1}s^{-1}$ and its activation energy is 71kJ/mol. Calculate the frequency factor and entropy of activation. Given: $\Delta n=1$. (6+4)
6. a) Prove that in Enzyme catalysis the order with respect to substrate changes from unity to zero at higher concentration.
   b) The rate of an enzyme catalyzed reaction and the substrate concentration are given as 2.3×10^{-4} M s^{-1} and 2.5×10^{-4}M respectively. Calculate the Michaleis-Menten constant if the limiting rate is found to be $8.92\times10^{-4}Ms^{-1}$. (6+4)
7. a) Chloro benzene on nitration undergoes two first-order parallel reactions to give ortho and para-chloronitrobenzene. Obtain the rate expression for each product.
   b) How is the ionic strength related to the concentration in 0.5 M Aluminium hydroxide solution**?** (7+3)
8. How are relaxation techniques and electric field jump methods used to study the kinetics of rapid reactions?

SECTION B

Answer any THREE questions. **(3 × 20 = 60)**

9. a) How is the fugacity of gases determined by graphical method?
   b) Explain the variation of chemical potential with temperature and pressure. (10+10)
10. a) State the principle of microscopic reversibility. How is it used to verify Onager's reciprocal relation?
    b) Explain the salient features of Debye and Einstein's theory of heat capacity of solids. (10+10)

11. a) Derive Maxwell-Boltzmann statistics for the most probable distribution.
    b) Obtain an expression for translational partition function. Calculate the molecular translational partition function for 1 mol of nitrogen gas at 27^0C and 1.013 x 10^{-5} Nm^{-2} assuming the gas behaves ideally. (10+10)
12. a) Define the rate of a reaction in the light of transition state theory and obtain an expression for the rate constant of the reaction of the type AB + CD → P, where P is a non-linear tetra atomic molecule.
    b) Explain the factors that determine the rates of reactions in solution. Obtain an expression to show the effect of dielectric constant of the medium on the rate constant and discuss the salient features of the equation with examples. (10+10)
13. a) Obtain the rate expression for a reversible reaction that follows first order in both the directions. Prove that the rate expression is similar to an irreversible first order reaction.
    b) How are kinetic parameters evaluated in an enzymatic reaction? Calculate the limiting rate of an enzyme catalysed reaction when the concentration of the enzyme is 3.45×10^{-7}M and the rate constant is $2.08\times10^{3}s^{-1}$. (12+8)
14. a) Discuss the kinetic features of the thermal decomposition of acetaldehyde using Rice-Herzfeld mechanism. Mention the significance of time and true order in this reaction.
    b) Derive equations for the rate constants of cationic and anionic polymerization reactions. (10+10)
