LOYOLA COLLEGE (AUTONOMOUS) CHENNAI – 600 034

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

THIRD SEMESTER – **NOVEMBER 2024**

PCH 3502 – THERMODYNAMICS AND CHEMICAL KINETICS

Date: 09-11-2024 Dept. No. Max. : 100 Marks

Time: 01:00 pm-04:00 pm

SECTION A

Answer ANY FOUR of the following **(4 x 10 = 40)**

1. (a) Predict the degrees of freedom in all regions of the phase diagram of a ternary system in which one compound forms a hydrate. (6)
   (b) Calculate the fugacity coefficient of ammonia at 500 K and 100 atm pressure, given that the gas obeys the equation of state P(V-b) = RT and b = 0.037 $dm^3\ mol^{-1}$. (4)
2. (a) Define fugacity. How is the fugacity of gases determined by graphical method? (7)
   (b) Calculate the molar residual entropy of a crystal in which the molecules can adopt seven orientations of equal energy at 0 K. (3)
3. (a) Discuss the entropy production and entropy flow in open systems. (5)
   (b) Explain the application of irreversible thermodynamics to biological systems with an example. (5)
4. (a) Deduce the relationship between partition function and entropy. (5)
   (b) Explain Einstein's theory of heat capacity of crystals. (5)
5. 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.
6. (a) Derive Michaleis-Menten equation using steady state hypothesis and discuss the influence of substrate concentration on the order of the reaction. (6)
   (b) The rate of an enzyme catalyzed reaction and the substrate concentration are given as $2.3\times10^{-4}\ Ms^{-1}$ and $2.5\times10^{-4}\ Ms^{-1}$, respectively. Calculate the Michaleis-Menten constant if the limiting rate is $8.92\times10^{-4}\ Ms^{-1}$. (4)
7. Discuss the kinetic features of the thermal decomposition of acetaldehyde using Rice-Herzfeld mechanism. Highlight the significance of time and true order in this reaction.
8. Explain the kinetics and mechanism of Free radical polymerisation process with an example.

SECTION B

Answer ANY THREE of the following **(3 x 20 = 60)**

9. (a) Derive Gibbs-Duhem equation. Mention its significances. (10)
   (b) Show that $(\partial\mu_i/\partial T)_{p,n_i} = -\bar{S}i$ (5)
   (c) The emf of the cell Pt, H_2(1atm) /HBr(m) // AgBr (s) / Ag (s) at 298 K is 0.3620 V. Calculate the mean activity coefficient of HCl at a molality of 0.004 and E^0 of the cell is 0.0707 V. (5)
10. (a) State the principle of microscopic reversibility. How can it be used to verify Onsager's reciprocal relation? (10)
    (b) Obtain the phenomenological equations and their cross coefficients for electrokinetic effects. (10)

11. (a) What are Bosons? Obtain the most probable distribution of indistinguishable particles using Bose-Einstein statistics. (10)

(b) Obtain the expression for rotational partition function. (5)

(c) Calculate the molecular rotational partition function for nitrogen gas at 27 ^{o}C. The moment of inertia of nitrogen is 13.9 x 10^{-47} Kg m^2.

(5)

12. (a) Discuss the Lindemann-Christiansen's theory of unimolecular reaction and mention the effect of time lag on the order of the reaction.

(8)

(b) Obtain an expression to study the influence of dielectric constant of the medium on the rate of reaction in solutions.

(7)

(c) Calculate the ionic strength of 1.5 M aluminium oxalate solution and show the relation between its ionic strength and concentration. (5)

13. (a) What is enzyme inhibition? Obtain an expression for the rate of competitive enzyme inhibition.

(8)

(b) A consecutive first order reactions of the type A $\rightarrow$ B $\rightarrow$ C have rate constants k_1 and k_2. Given that $[A_o]$ = 2 M, k_1 = 0.19 s^{-1} and k_2 = 0.1 s^{-1}. Calculate the time for the concentration of B to be maximum and the $[B]_{max}$.

(6)

(c) Discuss the construction of potential energy surface for a reacting system with an example and mention its importance. (6)

14. (a) Obtain an expression for the rate of anionic polymerisation reaction. (6)

(b) Discuss briefly the principle of Flow technique and Flash photolysis to study the kinetics of fast reactions. (10)

(c) Mention the significance of explosion and explosion limit with an example. (4)
