LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

THIRD SEMESTER – **NOVEMBER 2022**

PCH 3502 – THERMODYNAMICS AND CHEMICAL KINETICS

Date: 25-11-2022 Dept. No. Max. : 100 Marks

Time: 09:00 AM - 12:00 NOON

PART – A

Answer ALL questions. **(10×2=20 Marks)**

1. Account for the positive slopes observed in Ellingham's diagram.
2. Calculate the ionic strength of an aqueous solution of 0.2 M $BaCl_2$ and 0.1 M NaCl.
3. Write the conditions to be satisfied by cross coefficients of coupled and non-coupled reactions.
4. Evaluate $\ln 10^{25}!$ using Stirling's approximation.
5. Obtain the relation between partition function and entropy.
6. Calculate the number of molecules of oxygen present in 1 cm^3 of a reaction vessel at 27°C and at 1 atm.
7. Define rate of a reaction in the light of activated complex theory.
8. Calculate the limiting rate of an enzyme catalyzed reaction when the concentration of the enzyme is 3.45×10^{-7} M and the rate constant for the formation of product is 2.08×10^{3} s^{-1}.
9. Define chain length of a chain reaction with an example.
10. Compare the rate versus temperature plot of an enzyme catalyzed reaction with that of an explosive reaction.

PART – B

Answer any EIGHT questions. **(8×5=40 Marks)**

11. Derive Gibbs-Duhem equation. Mention its significance.
12. How is fugacity determined from equation of state?
13. Draw the phase diagram of a ternary system in which two compounds form hydrates and arrive at the degrees of freedom in all the regions.
14. Discuss the internal entropy production in chemical reactions.
15. Obtain Sackur-Tetrode equation for determining the entropy of monoatomic gases.
16. Calculate the vibrational partition function for nitrogen gas at 300 K, if the vibrational frequency is 2.360×10^{5} m^{-1}.
17. Discuss the construction of potential energy surface for a reacting system with an example. Mention its importance.
18. Calculate the rate constant k_1 for a non-linear triatomic molecule undergoing unimolecular reaction at 300 K. Given: $Z = 5\times10^{10}$ $M^{-1}s^{-1}$ and E_a = 60 kJ mol^{-1}.
19. Derive Michaelis-Menten mechanism using steady state hypothesis and predict the order at different concentration of the substrate.
20. Bring out the differences between Langmuir-Hinshelwood and Langmuir-Rideal mechanisms of a bimolecular surface adsorption.
21. The compound 2-bromo butane reacts with OH^- to form 2-butanol through S_N1 and S_N2 mechanisms parallely and their rate constants are found to be 1.5×10^{-6} s^{-1} and 3.2×10^{-5} $Lmol^{-1}s^{-1}$ respectively. Calculate the percentage of S_N2 reaction completed when the concentration of OH^- is (i) 2 M and (ii) 10^{-2} M.
22. Explain briefly the kinetics of cationic polymerization mechanism.

PART – C

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

23. a. Explain the variation of chemical potential with temperature and pressure.

    b. The emf of the cell, Pt, H_2 (1atm)/HCl//$AgCl_{(s)}$, Ag at 298 K is 0.3345 V. Calculate the mean activity coefficient of HCl at a molality of 0.1 m. (Given that E^o_{cell}= 0.2234 V). (7+3)

24. a. Discuss the validity and verification of Onsager equation in irreversible thermodynamics.

    b. What is meant by Seeback effect? (8+2)

25. a. Derive Maxwell-Boltzmann statistics for the most probable distribution.

    b. Calculate the thermodynamic probability of 25 distinguishable particles distributed in groups of 14, 6, 3 and 2. (7+3)

26. a. Discuss the effect of pressure on the kinetics of a unimolecular reaction. Mention its limitations.

    b. Obtain an expression for the rate constant, in the light of transition state theory, for the reaction between molecules AB and CD that form a linear activated complex.
    (5+5)

27. a. What is electrostriction? How is it caused? Give examples.

    b. The protein catalase catalyzes the reaction $2H_2O_2 \rightarrow 2H_2O + O_2$. The K_M value is 25×10^{-3}M and the maximum rate of the reaction is 0.64 Ms^{-1}. The total enzyme concentration and the initial substrate concentration are 0.016×10^{-6} M and 4.32×10^{-6} M, respectively. The presence of 4.8×10^{-6} M competitive inhibitor decreases the initial rate of 1.11×10^{-4} Ms^{-1} by a factor of 3.6. Calculate the equilibrium constant K_I for the binding between enzyme and the inhibitor.
    (5+5)

28. a. Derive the rate expression for the reaction β-glucose ⇌ α-glucose that follows first order in both the directions and prove that the rate expression is similar to an irreversible 1st order reaction.

    b. Discuss the principle of stopped flow technique to study the kinetics of fast reactions. (6+4)

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