LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

THIRD SEMESTER – **NOVEMBER 2018**

CH 3812 – CHEMICAL KINETICS

Date: 27-10-2018 Dept. No. Max. : 100 Marks

Time: 09:00-12:00

Part-A

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

1. What are the assumptions of conventional transition state theory?
2. Compare order and molecularity of a reaction.
3. Write the significance of the ratio of partition functions when two molecules react to form a non-linear activated complex.
4. Mention the significance of volume of activation.
5. Define the term Hammett acidity function.
6. Hydrogen peroxide decomposes in water by a first order process. Calculate the rate constant for the reaction if 0.156 mol dm^{-3}solution of H_2O_2 in water has an initial rate of 1.14×10^{-5} mol dm^{-3} s^{-1}.
7. What is the effect of temperature on the rate of enzymatic reactions?
8. Outline the graph relating the concentration and time of a simple consecutive reaction and explain.
9. Write the principle of relaxation technique to study fast reaction kinetics.
10. Distinguish between stationary and non-stationary chain reactions.

Part-B

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

11. Discuss the factors affecting the effectiveness of collision.
12. How is surface area of a solid determined using Langmuir adsorption isotherm?
13. Explain any two methods of determining order of a reaction.
14. Write a note on 'cage effect' with regard to the collision of molecules in solutions.
15. Calculate the rate constant for the decomposition of hydrogen iodide at 700 K, using collisiontheory formula. The energy of activation and the collision diameter of HI are 198.4 kJ mol^{-1} and 3.5 A^0 respectively.
16. Describe the equilibrium and steady state approach for homogeneous catalytic reactions with the help of potential energy diagram.
17. Write the importance of Skrabal plots in acid-base catalysis.
18. Explain the Langmuir-Hinshelwood mechanism of bimolecular surface reactions.
19. Derive an expression for relaxation rate constant and relaxation time for a fast reaction.
20. Differentiate competitive and non-competitive enzyme inhibition mechanisms.
21. Write a note on the first and second explosion limits for H_2-O_2 branched chain reaction.

22. Derive the expressions for the concentrations of reactants and products for a first order parallel reaction at time‘t’.

Part-C

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

23a. Derive the Eyring equation relating the thermodynamic parameters and rate constant of a reaction.

b. Draw and explain the potential energy surface diagram for the following reaction,

$H^{\alpha} + H^{\beta}\text{-}H^{\gamma} \rightarrow H^{\alpha}\text{-}H^{\beta} + H^{\gamma}$ (5+5)

24a. Discuss the Lindemann mechanism for atom and radical combination reaction in the presence of chaperon.

b. Distinguish between time and true order of a reaction. (6+4)

25a. Show that Bronsted catalytic law is a special case of linear free energy relations.

b. Write the BET equation and explain the terms involved in it. (6+4)

26a. The rate constant for the reaction, $S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$ is 1.6×10^{-5} mol^{-1} dm $^3s^{-1}$. Calculate the rate constant for the reaction in presence of 10^{-2} mol dm^{-3} of $BaCl_2$.

b. Explain the double sphere model for the influence of dielectric constant on the rate of an ion-ion reaction in solution. (4+6)

27a. Derive the Michaelis-Menten equation for single substrate enzymatic reactions.

b. The enzyme, protein catalase catalysing the decomposition of hydrogen peroxide has K_M and turnover number of 22×10^{-3} mol L^{-1} and 4×10^7 s^{-1} respectively. Calculate the maximum rate of the reaction if the total enzyme concentration is 10 nM. (7+3)

28a. Derive the Stern Volmer equation and explain its verification.

b. Explain the principle of flash photolysis for studying the kinetics of fast reactions. (5+5)

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