LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

FOURTH SEMESTER – **APRIL 2016**

CH 4807 - CHEMICAL KINETICS

Date: 25-04-2016 Dept. No. Max. : 100 Marks

Time: 09:00-12:00

Part – A

Answer **all** the questions **(10 × 2 = 20)**

1. Define orientation factor of a reaction based on collision theory.
2. The rate constant for a second order reaction is 3.33×10^{-2} dm^3 mol^{-1} s^{-1}. Calculate its half-life if the initial concentration of the reactant is 0.05 mol dm^{-3}.
3. Write the limitations of collision theory of reactions.
4. Distinguish between time and true order of a reaction.
5. What is electrostriction?
6. Why are conventional techniques not useful to study fast reactions?
7. Calculate the t_{max} for a consecutive reaction, A→ B→ C with rate constants of 0.3 min^{-1} and 0.2 min^{-1} for the first and second steps respectively.
8. Define degree of inhibition.
9. What is the effect of pH on an enzymatic reaction?
10. How are the kinetic parameters evaluated for an enzymatic reaction by Lineweaver-Burk plot?

Part – B

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

11. The pre-exponential term for a unimolecular gaseous reaction occurring at 300 ºC is 3.98×10^{13} s^{-1} and the energy of activation for this reaction at this temperature is 170 $kJmol^{-1}$. Determine $\Delta^{\neq}H$□ and $\Delta^{\neq}S$□ for the reaction.
12. Describe any one method for the determination of order of a reaction.
13. Using appropriate diagrams discuss the role of potential energy surfaces in reaction kinetics.
14. Explain the double sphere model for the influence of dielectric constant on the rate of an ion-ion reaction in solution.
15. Show that Hammett equation is a form of linear free energy relationship.
16. For a weak base, 2-nitroaniline (B) in 0.02 M $HClO_4$, the ratio of $[BH^+]$ to [B] is found to be 0.01. Calculate pK_{BH+} for 2-nitroanilinium ion.
17. Discuss the mechanism of reversible enzyme inhibition reactions.
18. Explain flash photolysis technique to study the kinetics of fast reactions.
19. Discuss the kinetics of thermal decomposition of acetaldehyde.
20. Derive Eyring equation connecting rate constant and partition functions of reactants.
21. Write the salient features of Langmuir-Hinshelwood mechanism for the surface catalysed reactions.
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)**

23 a. Explain the kinetics of unimolecular gas phase reaction with relevant derivation.

b. Bodenstein studied the kinetics of decomposition of gaseous hydrogen iodide and gave the values of specific reaction rates to be 3.52×10^{-7} and 3.96×10^{-2} dm^3 mol^{-1} s^{-1} at 556 and 781 K respectively. Calculate the energy of activation and frequency factor of the reaction. **(5+5)**

24 a. Predict the effect of increasing ionic strength on rates of the following reactions and estimate the sign of $\Delta^{\neq}S$ in each case.

$[Co(NH_3)_5Cl]^{2+} + OH^- \rightarrow [Co(NH_3)_5OH]^{2+} + Cl^-$

$CH_3Br + H_2O \rightarrow CH_3OH + H^+ + Br^-$

b. Discuss the factors determining rate of a reaction in solution. **(6+4)**

25 a. Differentiate Arrehenius and van't Hoff type intermediates.

b. Explain the importance of Skrabal plots in acid-base catalysis. **(5+5)**

26 a. Discuss the kinetic scheme for a quenching reaction and derive Stern-Volmer equation.

b. Write BET equation and mention the parameters in it. **(7+3)**

27 a. Explain the kinetics of single substrate enzymatic reaction.

b. The protein catalase that catalyses the decomposition of hydrogen peroxide has K_M and turnover number of 25×10^{-3} mol L^{-1} and 4×10^7 s^{-1} respectively. Calculate the maximum rate of the reaction if the total enzyme concentration is 1.6×10^{-8} M. **(7+3)**

28. Discuss the kinetics of branching chain reactions in detail.

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