LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION - **CHEMISTRY**

THIRD SEMESTER – **NOVEMBER 2013**

CH 3812/4807 - CHEMICAL KINETICS

Date : 04/11/2013 Dept. No. Max. : 100 Marks

Time : 9:00 - 12:00

Part-A

Answer all questions. Each question carries two marks.

1. Differentiate true order from time order.
2. What are the assumptions of transition state theory?
3. The $t_{1/2}$ of a reaction is halved as the initial concentration of the reactant is doubled. What is the order of the reaction?
4. What is electrostriction?
5. Predict the influence of ionic strength on the rate of the following reaction in solution,
   $S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$
6. Define: turnover number.
7. What are Arrhenius and van't Hoff intermediates?
8. Write the mechanism for the thermal decomposition of acetaldehyde.
9. What is capillary condensation?
10. State the principle of pulse radiolysis technique.

Part-B

Answer eight questions. Each question carries five marks.

11. Explain any two methods of determining order of a reaction.
12. The rate constant of a second-order reaction is $5.70\times10^{-5} dm^3mol^{-1}s^{-1}$ at 25°C and $1.64\times10^{-4} dm^3mol^{-1}s^{-1}$ at 40°C. Calculate the activation energy and Arrhenius pre-exponential factor.
13. Using appropriate diagrams discuss the role of potential energy surfaces in reaction kinetics.
14. At 30°C in 80% ethanol, the rate constants in $dm^3mol^{-1}s^{-1}$ for the hydrolysis of m-chloroethylbenzoate and p-methoxyethylbenzoate are 0.454 and 0.0114 respectively. Given that σ values of m-Cl and p-OMe are +0.37 and -0.27 respectively, calculate the reaction constant ρ.
15. Discuss Lindemann theory of unimolecular reactions.
16. Explain the factors determining the rate of a reaction in solution.
17. Write a note on Skrabal plots.
18. Explain the effect of temperature and pH on enzymatic reactions.

19. Write BET equation. Mention the terms involved. How is the equation verified?
20. Describe the salient features of H_2-Br_2 chain reactions.
21. Discuss the kinetics of consecutive reactions with relevant graph.
22. Explain flash photolysis technique for studying the kinetics of fast reactions.

Part-C

Answer four questions. Each question carries ten marks.

23 a) Compare the rate constants of collision theory and ARRT for the reaction between two atom

b) Calculate the number of collisions per second in 1 $cm^3$of oxygen at 27°C and 101.3 kPa pressure. (d_{O_2} is 2.92 A°) (6+4)

24. a) Derive an expression for the rate constant of reactions for the formation of linear and non-linearactivated complex on the basis of ARRT.

b) The second order gas phase reaction $H_2 + I_2 \rightarrow 2HI$ has the rate constant of $2.34\times10^{-2}dm^3mol^{-1}s^{-1}$ at 400□C. Its activation energy is 150 $kJmol^{-1}$. Calculate $\Delta^{\neq}H$□ and $\Delta^{\neq}S$□. (5+5)

25. a) Explain the double sphere model for the influence of dielectric constant on the rate of thereaction between ions in solution.

b) Write the significance of Taft equation. (6+4)

26. a) Explain Bronsted catalytic law.

b) Describe Langumir-Hinshelwood mechanism for a bimolecular surface reaction.(5+5)

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

b) The enzyme catalysed conversion of a substrate at 25□C has K_M of 0.035 mol L^{-1}. rate of the reaction is 1.15×10^{-3} mol $L^{-1}s^{-1}$ when the substrate concentration is0.0110 mol L^{-1}. What is themaximum rate of this enzymolysis? (7+3)

28. a) Derive Stern-Volmer equation.

b)Deduce the expression for relaxation time for the reaction type, $A + B \rightarrow C$, second order forward and first order backward. (5+5)

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