LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

THIRD SEMESTER – **APRIL 2014**

CH 3812/4807 - CHEMICAL KINETICS

Date : 10/04/2014 Dept. No. Max. : 100 Marks

Time : 01:00-04:00

Part-A

Answer *all* the questions. Each carries *two* marks.

1. Calculate the activation energy of a reaction whose rate constant increases four times by arise of 15 °C from 27 °C.
2. What is true order? How is it different from time order of a reaction?
3. Define electrostriction.
4. State Lindemann-Christiansen hypothesis of unimolecular reactions.
5. Predict the influence of ionic strength on the rate of the following reaction in solution, $[Co(NH_3)_5Cl]^{2+} + OH^- \rightarrow [Co(NH_3)_5OH]^{2+} + Cl^-$
6. Distinguish between Arrhenius andvan't Hoff intermediates.
7. What is meant by capillary condensation?
8. For the benzoylation of *p*-nitroaniline, the rate constant is 5.5×10^{-3} $dm^3mol^{-1}s^{-1}$at 25 °C. Find the rate constant for the benzoylation of aniline using the data, $\rho = -2.781$ and $\sigma_{p\text{-}NO2} = 0.78$.
9. Differentiate competitive from uncompetitive inhibition enzymatic reaction.
10. Mention any four relaxation methods used to study the kinetics of ultrafast reactions.

Part-B

Answer any *eight* questions. Each carries *five* marks.

11. In the reaction, $2NO + 2H_2 \rightarrow N_2 + 2H_2O$, a molecular mixture of gases at 336 mm Hg initial pressure, was half changed in 108 s and when the initial pressure was 288 mm Hg, itwas half changed in 147 s. Determine the order of the reaction.
12. Draw and explain the potential energy diagram for the reaction, $H_A + H_BH_C \rightarrow H_AH_B + H_C$.
13. A bimolecular gaseous reaction between like molecules with collision diameter of 200 pm, molar mass of 100 $gmol^{-1}$ has a steric factor equal to 1.00. Calculate Arrhenius pre-exponential factor at 100 °C.
14. Mention the significance of Taft equation.
15. Calculate the translational partition function for carbon monoxide in the standard state of $10^3mol.m^{-3}$ at 27 °C. What will be the molar free energy associated with translation?
16. Explain the factors that affect the rate of an enzymatic reaction.
17. Discuss the kinetic scheme for a bimolecular quenching process and hence derive Stern-Volmer equation.
18. Write a note on Skrabal plots.
19. Describe any one mechanism for a bimolecular surface reaction.
20. Deduce the expression for relaxation time for the reaction type, A + B → C, second order forward and first order backward.

21. 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 is 0.0110 mol L^{-1}. What is the maximum rate of this enzymolysis?
22. Explain the factors determining the rate of a reaction in solution.

Part-C

Answer any *four* questions. Each carries *ten* marks.

23. Explain the kinetics of unimolecular gas phase reactions with relevant derivations.
24a. Derive an expression for the rate constant of reactions for the formation of linear and non-linear activated complex on the basis of ARRT. (5)
b. The pre-exponential factor for a unimolecular gas reaction occurring at 300 °C is 3.98×10^{13} s^{-1} and the energy of activation for this reaction at this temperature is 170 KJmol^{-1}. Determine $\Delta S^{\neq}$ and $\Delta H^{\neq}$. (5)
25a. Explain the double sphere model for the influence of dielectric constant on the rate ofthe reaction between ions in solution. (6)
b. Write BET equation. How is the equation verified? (4)
26a. Explain how the acidity functions are used in the mechanism of acid-base catalysis.
b. Describe the salient features of H_2-Br_2 chain reactions. (5)
27a. Explain the kinetics of single substrate enzymatic reaction. (7)
b. How are the kinetic parameters evaluated for an enzymatic reaction? (3)
28a. Discuss the kinetics of consecutive reactions with relevant graph. (5)
b. Explain flash photolysis technique for studying the kinetics of fast reactions. (5)

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