LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

THIRD SEMESTER – **NOVEMBER 2017**

CH 3812– CHEMICAL KINETICS

Date: 09-11-2017 Dept. No. Max. : 100 Marks

Time: 09:00-12:00

Part-A

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

1. Define 'true order' of a reaction.
2. Mention the factors that affect the rate of a chemical reaction.
3. Calculate the activation energy of a reaction whose rate constant increases two times by a rise of 10 ℃ from a temperature of 27 ℃.
4. The rate constant for a second order reaction with equal concentration 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}.
5. What is meant by capillary condensation?
6. How does volume of activation affect the rate of a reaction insolution?
7. State Lindemann-Christiansen hypothesis of unimolecular reactions.
8. Define Hammett acidity function.
9. Write the mechanism for the thermal decomposition of acetaldehyde.
10. Why did conventional techniques fail in studying fast reactions?

Part-B

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

11. Derive the expression for collision number of a bimolecular reaction.
12. Explain the significance of potential energy surfaces with an example.

13a. The rate of a reaction between the aqueous solutions of two singly charged cations in anionic strength of 0.035 $moldm^{-3}$ is 2.42 $L^2mol^{-2}min^{-1}$. Find the rate constant at zero ionic strength using Bronsted-Bjerrum equation.

b. What is meant by secondary salt effect? (3+2)

14. Derive Stern – Volmer equation and explain how it can be verified.
15. 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.
16. Derive the expressions for the concentrations of A, B and C for a consecutive reaction, A→ B→ C.
17. Explain any one mechanism of bimolecular surface reactions.
18. A gas phase unimolecular reaction has energy of activation of 49.6 kJ mol^{-1}. At 55 ºC the rate constant for the reaction is 0.23 s^{-1}. Calculate the enthalpy and entropy of activation at 55 ºC.
19. Describe the influence of dielectric constant on the rate of ionic reactions in solution.
20. Explain the reversible enzyme inhibition reactions with suitable mechanism.
21. Distinguish between Arrhenius and van't Hoff intermediates formed in homogeneous catalytic reactions.
22. Derive the expression for relaxation rate constant and relaxation time for a fast reaction.

Part-C

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

23. a. Derive Eyring equation connecting rate constant and partition function of reactants.
    b. Compare the rate constant expressions obtained by transition state and collision theories for the reaction between two atoms. (5+5)
24. Differentiate the following: (a) Thermal and photchemical reactions
    (b) Physisorption and chemisorption (c) order and molecularity. (3+4+3)
25. a. Write a note on Skrabal plots.
    b. How is surface area of a solid determined using BET equation? (5+5)
26. a. Explain the kinetics of a combination reaction following energy transfer mechanism.
    b. Calculate the rate constant for a diffusion-controlled second order reaction between two non-ionic solutes A and B using Smoluchowski equation. Given: $r_A = 2.0$ Å, $r_B = 3.0$ Å, $D_A = 1.212 \times 10^{-9}$ m^2 s^{-1} and $D_B = 8.08 \times 10^{-10}$ m^2 s^{-1}. (7+3)

27a. Explain the effect of substrate concentration on the rate of an enzymatic reaction.
    b. In a typical Lineweaver-Burk plot of 1/rate vs 1/[S], the slope and Y- intercept are 40.0 and 2.0 respectively. Determine the maximum rate and K_M value if the concentration is in mmol/L and time in seconds. (7+3)

28 a. Discuss the kinetics of hydrogen-bromine thermal chain reaction.
    b. Show that the mathematical expression of rate constant for a simple first order and reversible first order reactions is the same. (7+3)

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