LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

THIRD SEMESTER – APRIL 2017

CH 920 – CHEMICAL KINETICS

Date: 02-05-2017 Dept. No. Max. : 100 Marks
Time: 09:00-12:00

Part-A

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

1. What is volume of activation? Mention its significance.
2. The rate constant for a second order reaction is 5.23×10^{-2} dm^3 $mol^{-1}s^{-1}$. Calculate its half-life if the initial concentration of the reactant is 0.03 mol dm^{-3}.
3. State Lindemann-Christiansen hypothesis of unimolecular reactions.
4. Write the assumptions of conventional transition state theory.
5. Define Hammett acidity function and mention its significance.
6. What is capillary condensation?
7. Distinguish between protropic and protolytic mechanisms in acid catalysis.
8. Write Taft equation and mention the terms involved in it.
9. Calculate the enthalpy of activation for a unimolecular reaction having activation energy of 22.5 kJ mol^{-1} at 60 ºC.
10. Write the principle of flow techniques in studying the kinetics of fast reactions.

Part-B

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

11. Explain any two methods for the determination of order of a reaction.
12. Discuss the kinetics of unimolecular reactions.
13. Derive the expression for Langmuir adsorption isotherm.
14. Explain the temperature jump method for studying the kinetics of fast reactions.
15. The molecular diameters of O_2 and H_2 are 3.39×10^{-8} and 2.47×10^{-8} cm respectively. When one gram of O_2 and 0.1 g of H_2 are mixed in a one litre flask at 27ºC, what will be the number of collisions per cubic cm per second? ($V = 10^3 cm^3$)
16. Differentiate van't Hoff and Arrhenius intermediates formed in the homogenous catalytic reaction.
17. Explain the importance of Skrabal plots in acid-base catalysis.
18. 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.
19. Discuss the kinetics of hydrogen-chlorine chain reaction.
20. Distinguish between physisorption and chemisorption with suitable examples.
21. Discuss the kinetics of quenching of fluorescence.
22. Derive the expressions for the concentrations of A, B and C for a first order parallel reaction, A giving two parallel products, B and C at time t.

Part-C

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

23 a. Explain time and true order of a reaction with relevant graphs.

b. Using appropriate diagrams discuss the role of potential energy surfaces in reaction kinetics.

(5+5)

24a. Derive Eyring equation for transition state theory of reaction rates.

b. Write the limitations of collision theory. **(6+4)**

25a. Explain the double sphere model for the influence of dielectric constant on the rate of an ion-ion reactions in solution.

b. The rate of a reaction between X^{2-} and Y^{+} has been investigated in aqueous solution at 298 K and the second order rate constant at zero ionic strength is found to be 1.8 $M^{-1}s^{-1}$. What is the second order rate constant when the ionic strength of the medium is 2×10^{-4}M? **(7+3)**

26a. Explain the kinetics of single substrate enzymatic reaction.

b. The protein catalase catalysing the decomposition of hydrogen peroxide has K_M and turnover number of 28×10^{-3} $molL^{-1}$ and 3.5×10^{6} s^{-1}, respectively. Calculate the maximumrate of the reaction if the total enzyme concentration is 14×10^{-9} M. **(7+3)**

27a. Explain flash photolysis technique to study the kinetics of fast reactions.

b. Explain the kinetics of consecutive reactions with relevant graph. **(5+5)**

28 a. Discuss the kinetics of branched chain explosion reactions.

b. Explain any one mechanism for bimolecular surface reactions with an example.

(5+5)

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