LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

THIRDSEMESTER – APRIL 2018

CH 3812- CHEMICAL KINETICS

Date: 26-04-2018 Dept. No. Max. : 100 Marks

Time: 09:00-12:00

Part-A

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

1. Compare time and true order of a reaction.
2. Mention the limitations of collision theory.
3. Calculate the enthalpy of activation for a bimolecular reaction having activation energy of 49.5 kJ mol^{-1} at 55 ℃.
4. Define volume of activation.
5. Write Taft equation and mention the terms involved in it.
6. Distinguish between protolytic and prototropic mechanisms in acid-base catalysis.
7. Define Hammett acidity function. Mention its significance.
8. What is capillary condensation?
9. Outline the graph relating the concentration and time of a simple consecutive reaction, A→B→C
10. State the principle of stopped flow technique used in studying the kinetics of fast reactions.

Part-B

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

11. Describe any two methods of determining the order of a reaction.
12. Using appropriate diagrams discuss the role of potential energy surfaces in reaction kinetics.
13. Derive Eyring equation for transition state theory of reaction rates.
14. Consider the following reaction, $NH_4^+{}_{(aq)} + NO_2^-{}_{(aq)} \rightarrow N_{2(g)} + 2H_2O_{(l)}$, at 25°C. Determine the rate law and rate constant for the reaction using the following data.

$[NH_4^+]$, mol/L	$[NO_2^-]$, mol/L	Rate, mol/L/s
0.24	0.10	7.2×10^{-6}
0.12	0.10	3.6×10^{-6}
0.12	0.15	5.4×10^{-6}

15. Derive the general equation for unimolecular reactions using Lindemann-Hinshelwood mechanism.
16. Explain the effect of added salt on the rates of ionic reactions.
17. Describe Eley-Rideal mechanism of bimolecular surface reactions.
18. What are Skrabal plots? Mention their significance.

19. Differentiate Arrhenius and van't Hoff intermediates formed in homogeneous catalytic reactions.

20. Outline the effect of pressure and temperature on a branched chain reaction and explain its explosion regions.

21. Derive Stern-Volmer equation for quenching of fluorescence.

22. Discuss any two factors that affect the rate of enzymatic reactions.

Part-C

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

23a. Calculate the number of collisions per second in 1 cm^3 of nitrogen, if there are 2.45×10^{19} molecules cm^{-3} at 27 ℃. (molecular diameter of nitrogen is 2.92×10^{-8} cm).

b. Compare the rate constants calculated by TST and collision theory for the reaction between any two atoms. (3+7)

24a. Describe the influence of dielectric constant on the rate of ionic reactions in solution.

b. Compare order and molecularity of a reaction. (6+4)

25a. Show that Bronsted catalytic law is a special form of linear free energy relationship.

b. Derive Langmuir adsorption isotherm. (5+5)

26a. Derive Michaelis-Menten equation for single substrate enzymatic reaction.

b. Distinguish between chemisorption and physisorption. (7+3)

27a. Derive the expressions for the concentrations of A, B and C for a first order parallel reaction, where A gives two parallel products, B and C at time t.

b. Write the mechanistic steps for the thermal hydrogen-bromine chain reaction. (7+3)

28a. Derive an expression for relaxation time of a first order reaction of the type $A \rightleftharpoons B$.

b. Explain flash photolysis technique for studying the kinetics of fast reactions. (5+5)

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