# LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

THIRD SEMESTER – **APRIL 2016**

**CH 3812 – CHEMICAL KINETICS**

Date: 27-04-2016 Dept. No. Max. : 100 Marks

Time: 09:00-12:00

## PART-A

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

1. Define true order of a reaction.
2. Calculate the energy of activation if the rate constant for a reaction is doubled when the temperature increases from 25 ºC to 40 ºC.
3. What are the factors that determine the effectiveness of collisions?
4. The rate constant for the reaction, $H^+ + OH^- \rightarrow H_2O$ is $1.3 \times 10^{11}$ $dm^3\ mol^{-1}\ s^{-1}$. Calculate the half-life for the neutralisation process if $[H^+] = [OH^-] = 0.1$ M.
5. Compare order and molecularity of a reaction.
6. The pKa values of *p*-chlorobenzoic acid and benzoic acid are 3.98 and 4.19 respectively. Calculate the substituent constant (σ) for *p*-Cl. (Given: reaction constant = 1).
7. What is degree of inhibition? Mention its significance.
8. Distinguish between protolytic and prototropic mechanisms of acid-base catalysis.
9. What is steady state principle?
10. Write the principle of relaxation technique to study the kinetics of fast reactions.

## PART-B

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

11. Explain van't Hoff and half-life methods of determining the order of a reaction.
12. Calculate the collision number for the reaction between one mole of hydrogen and one mole of iodine at 700 K and one atmospheric pressure. Given that the diameters of hydrogenand iodine are 2.2 and 4.6 Å respectively.
13. Explain Lindemann hypothesis of unimolecular reactions.
14. How does ionic strength of the medium affect the rate of a reaction between ions in solutions?
15. Write BET equation for multilayer adsorption and explain the terms in it.
16. Describe Rideal-Eley mechanism for a bimolecular surface reaction with an example.
17. Discuss the mechanism of reversible enzyme inhibition reaction.
18. Derive an expression for the time at which concentration of B is maximum in terms of rate constants of first and second steps for a consecutive reaction, $A \rightarrow B \rightarrow C$.
19. Explain the importance of Skrabal plots in acid-base catalysis.
20. Derive Stern-Volmer equation.
21. Write the principle of flow techniques and explain any one flow method to study the kinetics of fast reactions.
22. Write a note on first and second explosion limits for $H_2$-$O_2$ branched chain reaction.

## PART-C

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

23.a. Compare the rate constant expressions obtained by transition state and collision theories for the reaction between two atoms. (5)

b. Calculate $\Delta^{\#}G^{o}$ and $\Delta^{\#}S^{o}$ for a bimolecular reaction having activation energy of 111.0 KJ $mol^{-1}$ at 500 K. (Given: Arrhenius parameter, $A = 2\times10^{9}$ L $mol^{-1}s^{-1}$). (5)

24 a. Discuss the effect of dielectric constant on the rate of reactions in solution. (7)

b. What is volume of activation? Mention its significance. (3)

25 a. Draw and explain the potential energy diagrams for catalytic reactions proceeding through Arrehenius and van't Hoff type intermediates. (5)

b. Show that Bronsted catalytic law is a special form of linear free energy relationship. (5)

26. Explain the kinetics of photochemical hydrogen-chlorine chain reaction.

27. Discuss the influence of substrate concentration and pH on the rate of enzymatic reactions.

28 a. What is capillary condensation? (3)

b. Derive an expression for relaxation time for a first order reaction of type $A \rightleftharpoons B$. (7)

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