LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

THIRD SEMESTER – NOVEMBER 2016

CH 3812 - CHEMICAL KINETICS

Date: 07-11-2016   Dept. No.   Max. : 100 Marks
Time: 09:00-12:00

Part-A

Answer ALL questions.   (10 × 2= 20)

1. Define orientation factor of a reaction based on collision theory.
2. At 327   , the rate constant of a first order reaction is 1.6×10^{-5} s^{-1}. When the temperature is increased by 100   , the value of rate constant increases to 6.36×10^{-3} s^{-1}. Calculate the activation energy for the reaction.
3. Write the limitations of collision theory of reactions.
4. What are secondary isotope effects?
5. Define electrostriction.
6. For the benzoylation of p-nitroaniline, the rate constant is 5.5×10^{-3} dm^3 mol^{-1} s^{-1}
   at 25 C. Find the likely rate constant for the benzoylation of aniline using the data,
   ρ = -2.781 and σ for p-NO$_2$ = 0.78.
7. What is Hammett acidity function? Mention its significance.
8. Write the mechanism for the thermal decomposition of acetaldehyde.
9. Compare competitive from noncompetitive enzyme inhibition reactions.
10. Substantiate as to why the conventional techniques failed in studying fast reactions.

Part-B

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

11. The pre-exponential factor for a unimolecular reaction occurring at 200   is 2.75×10^{15} s^{-1}.
    Calculate $\Delta^{\neq}H$ and $\Delta^{\neq}S$ for the reaction. (E$_a$ =85.2 KJ mol^{-1})
12. Discuss the need for potential energy surfaces.
13. Derive Eyring equation for transition state theory of reaction rates.
14. Discuss Lindemann mechanism for atom and radical combination reaction in the presence of chaperon.
15. Explain the influence of ionic strength on the rate of the chemical reactions in solution.
16. The results for the rate of a reaction between two reactants X and Y at 300 K are   shown below.
    Deduce the overall order and rate constant of the reaction.

[X], mol/L	[Y], mol/L	Rate, mol/L/s
1.0×10^{-5}	1.0×10^{-3}	8.7×10^{-4}
2.0×10^{-5}	1.0×10^{-3}	3.48×10^{-3}
4.0×10^{-5}	5.0×10^{-3}	6.96×10^{-2}

17. Discuss the kinetics of quenching of fluorescence.
18. Explain the importance of Skrabal plots in acid-base catalysis.
19. Deduce the expression for relaxation time for the reaction of the type, A + B $\rightleftharpoons$ C, which follows second   order kinetics in the forward and first order kinetics in the reverse direction.
20. Write BET equation and explain the terms involved in it.
21. How do pH and temperature affect the rate of enzymatic reactions?
22. Explain the kinetics of hydrogen-bromine chain reaction.

Part-C

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

23a. Calculate the translational partition function for carbon monoxide in the standard state of 10^3 mol m^{-3} at 27°C. What will be the molar free energy associated with translation?   **(5+5)**

  b. Compare the rate constants of collision theory and ARRT for the reaction between two atoms.

24. Explain the effect of dielectric constant on the rate of reactions in solution.

25. Discuss the kinetic scheme for a single substrate enzymatic reaction and explain how the kinetic parameters can be evaluated.

26a. Describe any one mechanism for a bimolecular surface reaction.   **(5+5)**

  b. The energy of activation at 1000 K for the decomposition of hydrogen iodide on gold surface which follows zero order kinetics is 104.6 kJ mol^{-1}. If the number of adsorbed molecules per cm^2 is 10^{15}, Calculate the rate of decomposition at 1000 K.

27a. Differentiate Arrhenius from van't Hoff type intermediates.   **(5+5)**

  b. Write a note on Bronsted catalytic law.

28 a. Discuss the kinetics of consecutive reactions with relevant graph.   **(5+5)**

  b. Explain the flash photolysis technique for studying the kinetics of fast reactions.

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